

*Supporting Information for*

**Electronic Structure and Bonding in Iron(II) and Iron(I) Complexes Bearing Bisphosphine Ligands of Relevance to Iron-Catalyzed C-C Cross-Coupling**

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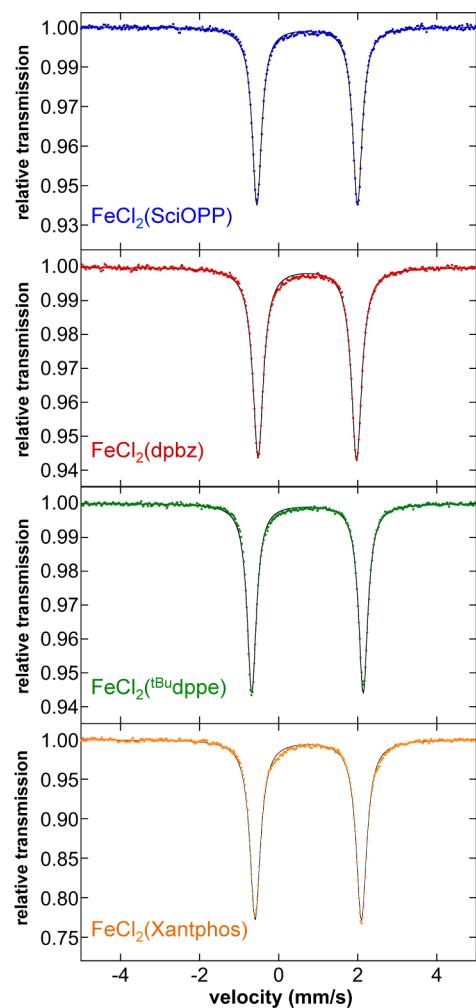
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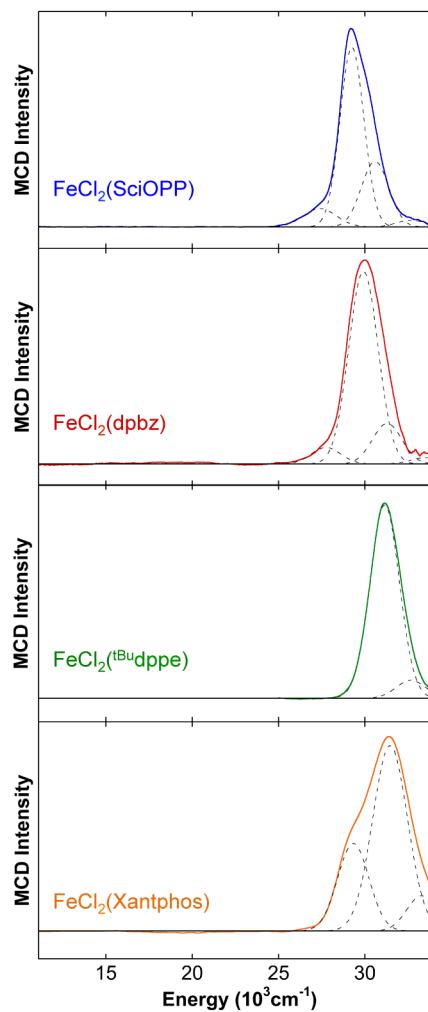
## 1. Supplementary Data

### 1.1 Mössbauer Spectra

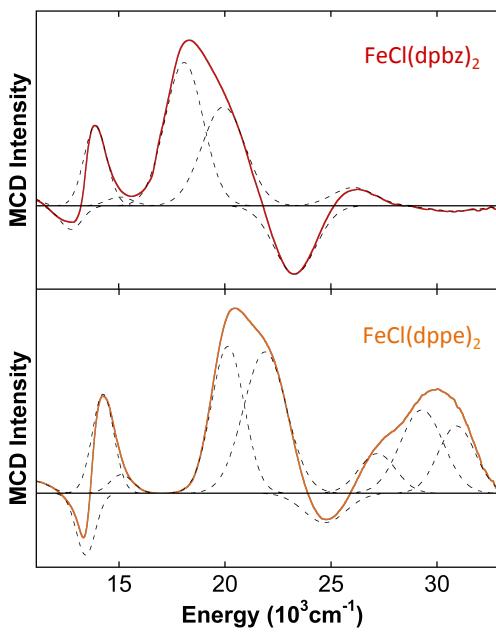


**Figure S1.** 80 K, Solid-state  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{FeCl}_2(\text{bisphosphine})$  complexes. The best-fit parameters for each complex are given in the manuscript in Table 1.

## 1.2 UV-Vis MCD Spectra

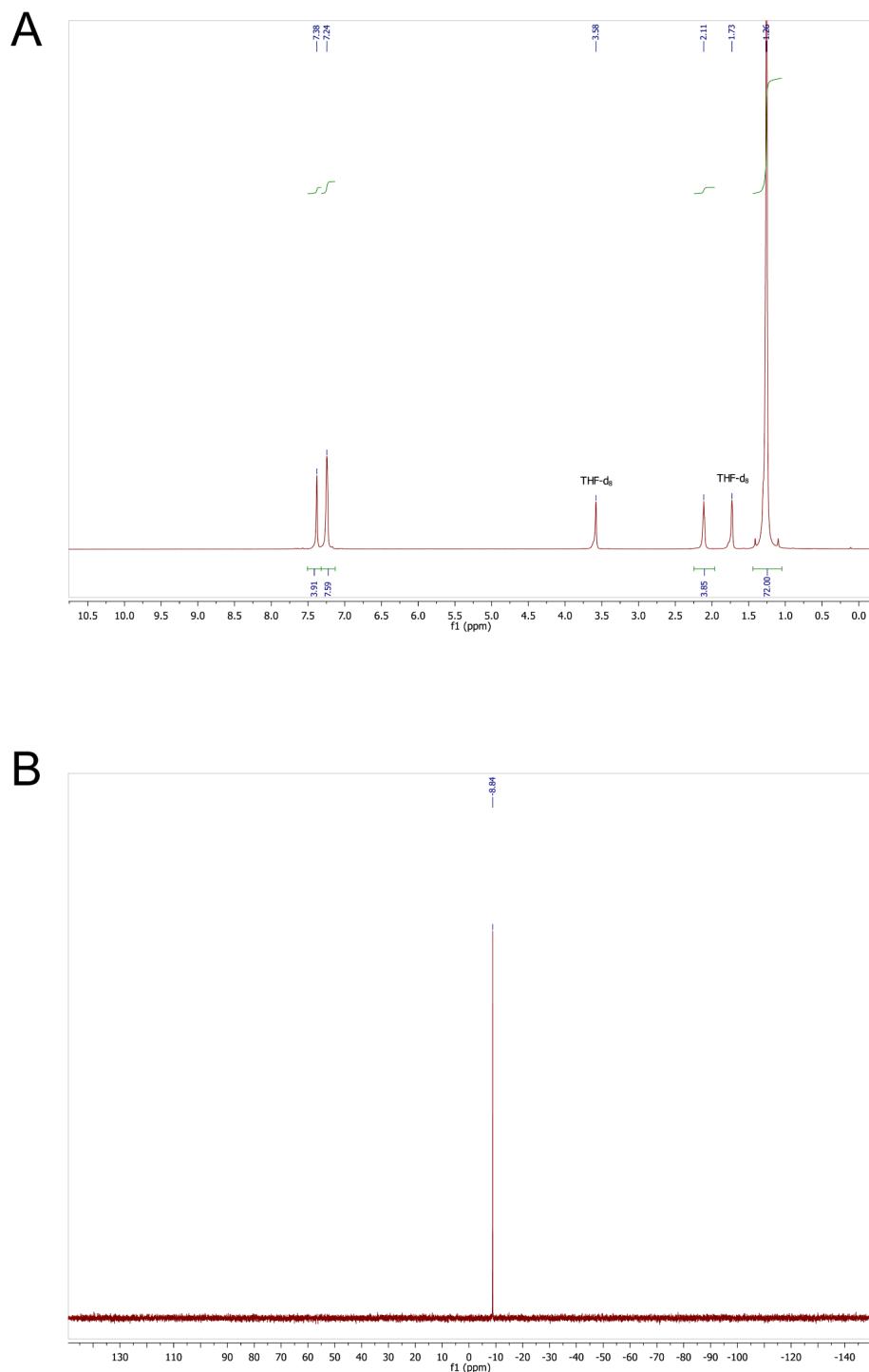


**Figure S2.** UV-Vis MCD spectra of  $\text{FeCl}_2$ (bisphosphine) complexes. Data (solid lines) and individual transition Gaussian fits (dashed lines) are given for each complex. The  $\text{FeCl}_2(\text{SciOPP})$  spectrum was collected at 15 K and 7 T whereas all other spectra were collected at 5 K and 7 T. All spectra were collected in 6:1, toluene-d<sub>8</sub>:benzene-d<sub>6</sub> except for  $\text{FeCl}_2(\text{Xantphos})$  which was collected on a solid mull sample.



**Figure S3.** 5 K, 7 T UV-Vis MCD spectra of  $\text{FeCl}(\text{dpbz})_2$  and  $\text{FeCl}(\text{dppe})_2$ . Data (solid lines) and individual transition Gaussian fits (dashed lines) are given for each complex. Spectra were collected in 6:1, toluene-d<sub>8</sub>:benzene-d<sub>6</sub>

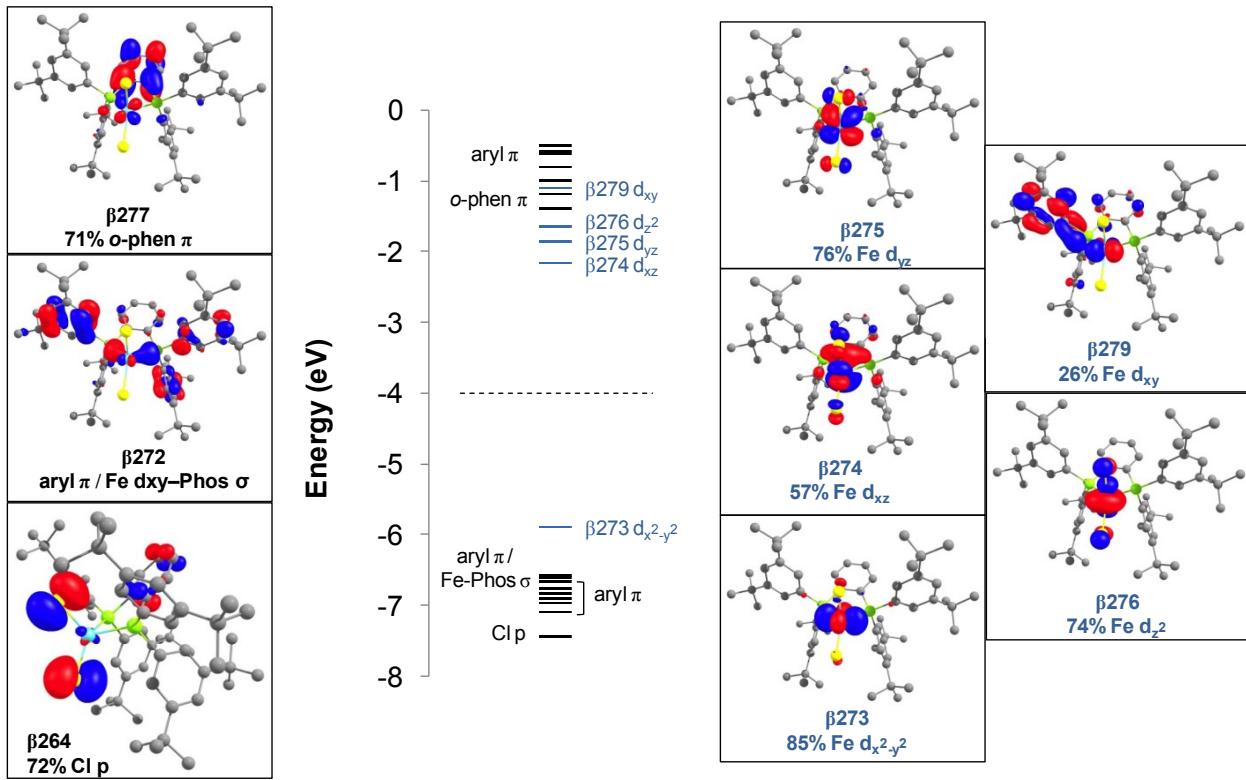
### 1.3 NMR Spectra



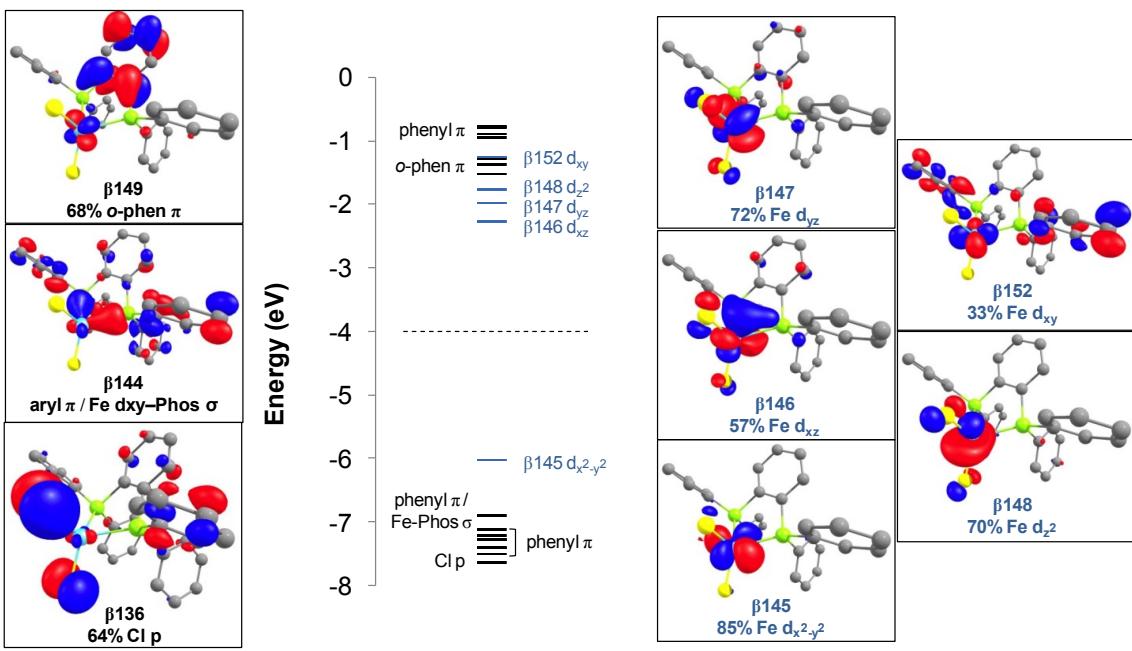
**Figure S4.** (A)  $^1\text{H}$  NMR (400 MHz) and (B)  $^{31}\text{P}$  NMR (400 MHz) of  $^{\text{tBu}}\text{dppe}$ .

## 2. DFT Analysis

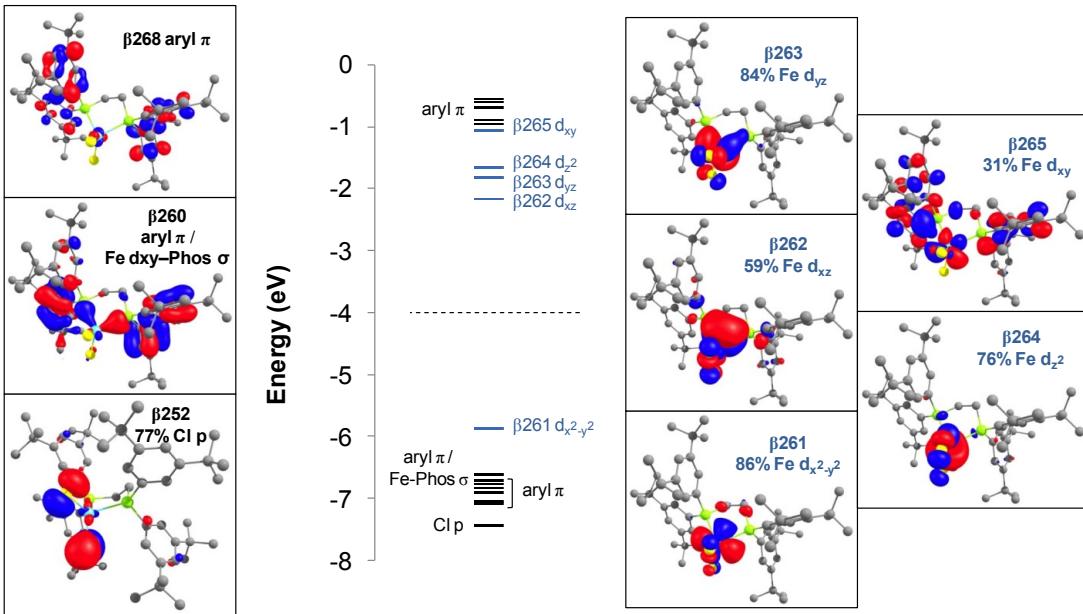
### 2.1 Calculated MO Energy Level Diagrams



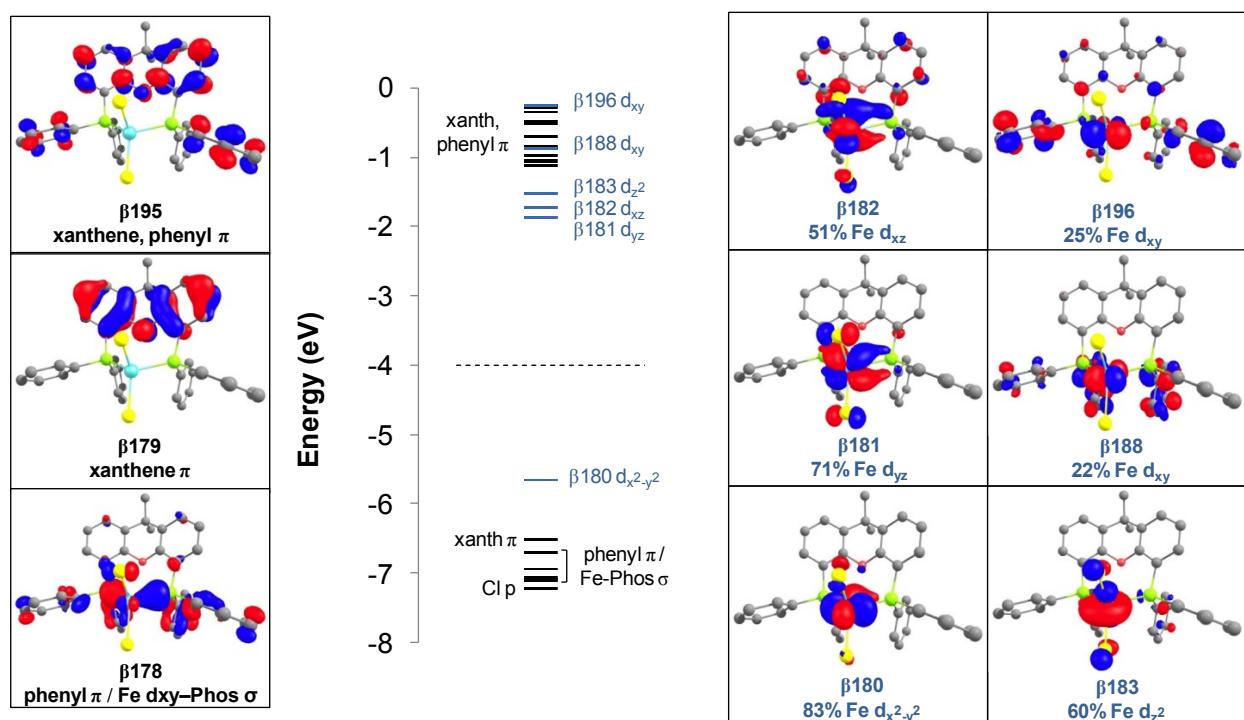
**Figure S5.** Calculated FMO energy level diagram for  $\text{FeCl}_2(\text{SciOPP})$  and selected orbital depictions.



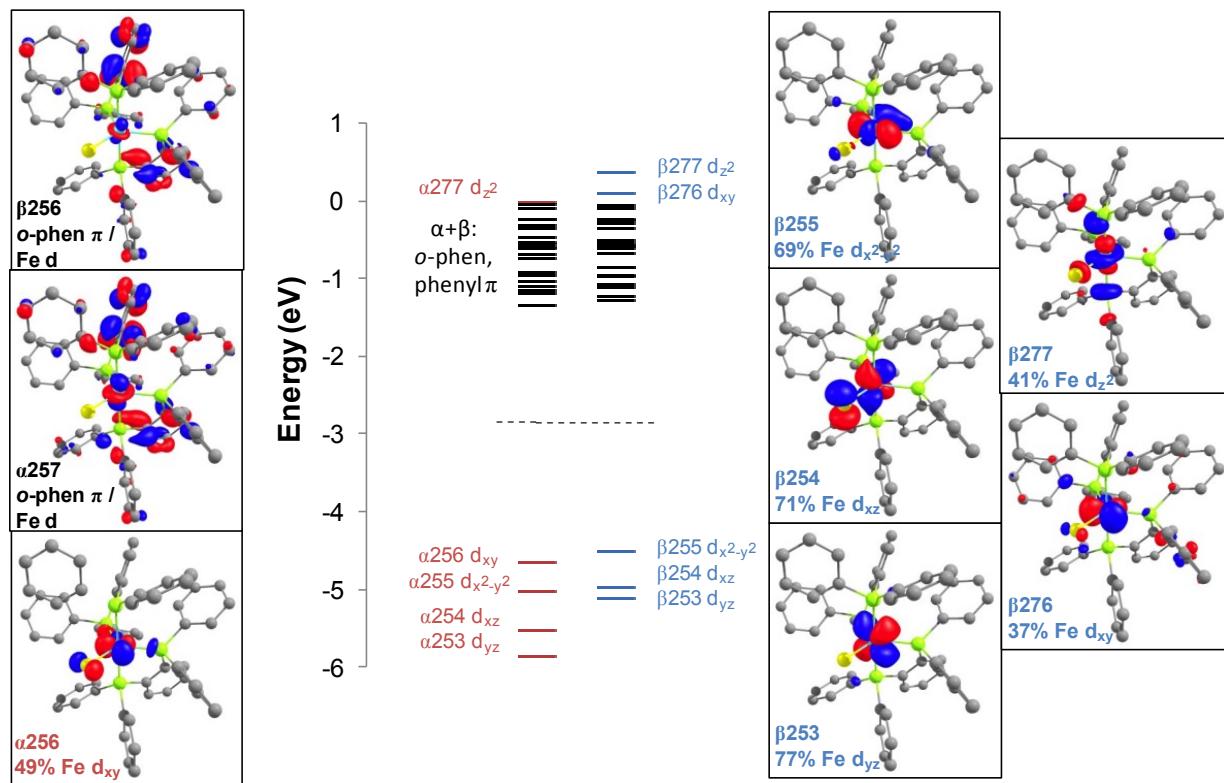
**Figure S6.** Calculated MO energy level diagram for  $\text{FeCl}_2(\text{dpbz})$  and selected orbital depictions.



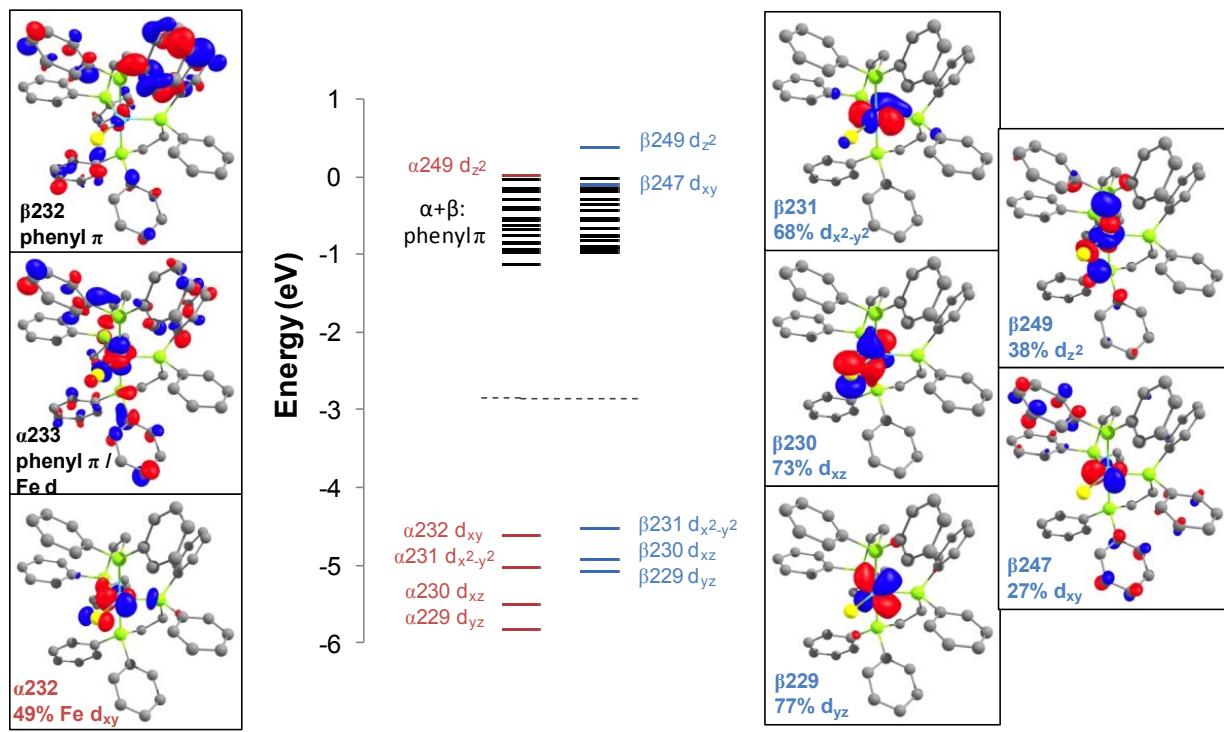
**Figure S7.** Calculated FMO energy level diagram for  $\text{FeCl}_2(^{\text{tB}}\text{u}\text{dppe})$  and selected orbital depictions.



**Figure S8.** Calculated FMO energy level diagram for  $\text{FeCl}_2(\text{Xantphos})$  and selected orbital depictions.



**Figure S9.** Calculated FMO energy level diagram for  $\text{FeCl}(\text{dpbz})_2$  and selected orbital depictions.



**Figure S10.** Calculated FMO energy level diagram for  $\text{FeCl}(\text{dppe})_2$  and selected orbital depictions.

## 2.2 TD-DFT Assignments of CT Transitions for $\text{FeCl}_2(\text{bisphosphine})$ Complexes

**$\text{FeCl}_2(\text{SciOPP})$ .** Observed transitions in the UV-Vis MCD spectrum of  $\text{FeCl}_2(\text{SciOPP})$  have been assigned using TD-DFT calculations. The high energy CT transitions observed by UV-Vis MCD are quite mixed, with dominant transition character in the bands at  $27390\text{ cm}^{-1}$  and  $29250\text{ cm}^{-1}$  deriving from MLCT within the  $\alpha$  manifold from  $\text{Fe d}_{xy}$  to low lying acceptor MOs of *o*-phen  $\pi$  character. The band at  $30590\text{ cm}^{-1}$  is composed of mixed  $\alpha$  (MLCT) and  $\beta$  (LMCT) character, with  $\text{Fe d}_{xy} \rightarrow o\text{-phen } \pi$  character in the  $\alpha$  manifold and aryl  $\pi$  /  $\text{Fe d}_{xy}\text{-Phos } \sigma \rightarrow \text{Fe d}_{xz}/\text{d}_{yz}$  in the  $\beta$  manifold. The last observed CT transition at  $32685\text{ cm}^{-1}$  is again mixed but the dominant transition character is LMCT from aryl  $\pi$  based MOs to  $\text{Fe d}_{xz/yz}$ .

**$\text{FeCl}_2(\text{dpbz})$ .** Observed transitions in the UV-Vis MCD spectrum of  $\text{FeCl}_2(\text{dpbz})$  have been assigned using TD-DFT calculations. Assignments of the high energy CT transitions of  $\text{FeCl}_2(\text{dpbz})$  are similar to those of  $\text{FeCl}_2(\text{SciOPP})$  reflecting the consistent *o*-phen backbone structure in both complexes. The transitions observed at  $27750\text{ cm}^{-1}$  and  $29920\text{ cm}^{-1}$  are dominated by transitions in the  $\alpha$  manifold bearing  $\text{Fe d}_{xy} \rightarrow o\text{-phen } \pi$  transition character. The band at  $31290\text{ cm}^{-1}$  is composed of mixed  $\alpha$  (MLCT) and  $\beta$  (LMCT) character, with  $\text{Fe d}_{xy} \rightarrow o\text{-phen } \pi$  character in the  $\alpha$  manifold and phenyl  $\pi$  /  $\text{Fe d}_{xy}\text{-Phos } \sigma \rightarrow \text{Fe d}_{xz}/\text{d}_{yz}$  character in the  $\beta$  manifold. The highest energy transition at  $33530\text{ cm}^{-1}$  is dominantly composed of  $\beta$  LMCT character in the form of phenyl  $\pi$  /  $\text{Fe d}_{xy}\text{-Phos } \sigma \rightarrow \text{Fe d}_{xz}/\text{d}_{yz}$ .

**$\text{FeCl}_2(^{\text{tBu}}\text{dppe})$ .** Observed transitions in the UV-Vis MCD spectrum of  $\text{FeCl}_2(^{\text{tBu}}\text{dppe})$  have been assigned using TD-DFT calculations. Unlike both  $\text{FeCl}_2(\text{SciOPP})$  and  $\text{FeCl}_2(\text{dpbz})$ , the CT region for  $\text{FeCl}_2(^{\text{tBu}}\text{dppe})$  is void of transitions below  $30000\text{ cm}^{-1}$ , reflecting the lack of backbone  $\pi$ -based MOs in the case of  $\text{FeCl}_2(^{\text{tBu}}\text{dppe})$  and the fact that LLCT transitions bearing minimal Fe d character are predicted by TD-DFT to be dominant in this region. The two experimental CT transitions at  $31150\text{ cm}^{-1}$  and  $32670\text{ cm}^{-1}$  are both dominated by  $\beta$  LMCT (aryl  $\pi$  /  $\text{Fe d}_{xy}\text{-Phos } \sigma \rightarrow \text{Fe d}_{xz}/\text{d}_{yz}$ ) transition character.

**$\text{FeCl}_2(\text{Xantphos})$ .** Observed transitions in the UV-Vis MCD spectrum of  $\text{FeCl}_2(\text{Xantphos})$  have been assigned using TD-DFT calculations. The high energy CT transitions observed by UV-Vis MCD are quite mixed, with dominant transition character in the band at  $29330\text{ cm}^{-1}$  deriving from LMCT in the beta manifold with phenyl  $\pi$  /  $\text{Fe d}_{xy}\text{-Phos } \sigma \rightarrow \text{Fe d}_{xz}$  transition character. The two higher energy transitions at  $31460\text{ cm}^{-1}$  and  $33280\text{ cm}^{-1}$  derive intensity from  $\alpha$  MLCT to low lying ligand-based acceptor orbitals ( $\text{Fe d}_{x2-y2} \rightarrow \text{xanth, phenyl } \pi$ ).

## 2.3 Optimized Geometry Coordinates

### 2.3.1 FeCl<sub>2</sub>(SciOPP) optimized with uPBE/PBE/TZVP (toluene PCM)

26	4.154518000	18.770086000	5.727238000
17	2.057797000	18.878341000	4.924956000
17	5.622381000	20.412095000	5.391102000
15	3.986997000	17.906150000	7.978061000
15	4.966765000	16.552091000	5.251707000
6	3.689280000	16.086356000	7.728498000
6	3.001567000	15.308363000	8.672655000
6	2.795523000	13.944309000	8.456212000
6	3.265745000	13.344607000	7.284009000
6	3.933564000	14.112248000	6.327703000
6	4.156914000	15.481746000	6.538877000
6	2.599075000	18.424342000	9.090831000
6	2.811733000	18.847189000	10.412751000
6	1.737011000	19.264249000	11.207662000
6	0.447349000	19.238557000	10.643639000
6	0.205748000	18.832115000	9.325095000
6	1.308699000	18.434419000	8.550713000
6	5.492435000	17.990361000	9.051227000
6	6.335197000	19.102163000	8.919866000
6	7.441241000	19.260789000	9.769896000
6	7.666678000	18.272804000	10.740621000
6	6.843296000	17.145071000	10.893457000
6	5.751604000	17.014609000	10.024357000
6	4.586666000	15.673345000	3.664898000
6	3.316076000	15.865359000	3.105831000
6	2.954369000	15.224208000	1.912298000
6	3.909163000	14.400538000	1.291655000
6	5.194789000	14.202015000	1.820295000
6	5.519715000	14.851749000	3.021803000
6	6.788079000	16.323172000	5.454259000
6	7.615145000	17.238126000	4.796255000
6	9.012183000	17.080223000	4.803574000
6	9.539190000	15.991465000	5.508880000
6	8.733514000	15.070940000	6.207216000
6	7.345770000	15.250068000	6.167341000
6	1.922191000	19.745820000	12.657597000
6	3.393540000	19.709815000	13.103020000
6	1.416636000	21.201279000	12.779793000
6	1.106757000	18.840775000	13.608352000
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6	-2.290357000	19.240790000	9.697843000
6	-1.527149000	17.408801000	8.181721000
6	-1.222337000	19.819247000	7.510691000
6	8.395515000	20.462924000	9.662307000

6	8.427704000	21.216796000	11.011030000
6	9.816187000	19.954918000	9.328055000
6	7.964255000	21.453207000	8.568008000
6	7.146678000	16.122740000	12.003593000
6	7.091849000	16.833676000	13.375031000
6	8.557863000	15.531447000	11.794236000
6	6.136601000	14.963214000	12.022363000
6	1.551291000	15.458119000	1.325800000
6	1.320216000	14.673142000	0.023595000
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6	1.371137000	16.963820000	1.026302000
6	6.244964000	13.309796000	1.134551000
6	5.728578000	12.697671000	-0.178276000
6	6.635330000	12.155591000	2.085290000
6	7.500580000	14.151979000	0.814168000
6	9.394068000	13.905017000	6.962764000
6	8.367794000	13.041478000	7.715533000
6	10.138974000	13.002494000	5.952619000
6	10.405650000	14.460493000	7.989817000
6	9.893226000	18.093369000	4.052974000
6	11.387511000	17.738726000	4.128210000
6	9.478890000	18.127131000	2.564151000
6	9.690630000	19.496192000	4.668365000
1	2.605566000	15.781892000	9.573387000
1	2.256516000	13.352302000	9.198588000
1	3.097676000	12.280715000	7.105213000
1	4.267134000	13.649851000	5.396315000
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1	6.128117000	19.835263000	8.139043000
1	8.524141000	18.385020000	11.408319000
1	5.090278000	16.152755000	10.105116000
1	2.613426000	16.536431000	3.605370000
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1	6.510351000	14.725276000	3.461398000
1	7.162917000	18.086684000	4.278390000
1	10.620164000	15.850791000	5.525401000
1	6.686127000	14.556138000	6.687296000
1	3.808358000	18.690977000	13.067054000
1	3.470942000	20.062834000	14.142171000
1	4.027171000	20.360904000	12.482336000
1	1.981378000	21.869956000	12.113260000
1	1.541174000	21.560414000	13.813196000
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1	0.035009000	18.851800000	13.363488000
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1	1.455553000	17.798367000	13.554017000

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1	0.366391000	17.149136000	0.615367000
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1	5.460808000	13.471378000	-0.913471000
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1	7.391550000	11.511547000	1.609942000
1	5.760418000	11.533760000	2.328481000
1	7.254541000	14.981040000	0.133983000
1	8.263676000	13.524069000	0.328269000
1	7.946301000	14.582200000	1.722390000
1	7.806188000	13.627856000	8.458661000
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1	7.645219000	12.570725000	7.031895000

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1	10.624283000	12.164600000	6.477005000
1	10.918338000	13.556484000	5.409588000
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1	10.881165000	13.632338000	8.537730000
1	9.906132000	15.114919000	8.719453000
1	11.757041000	17.732861000	5.164857000
1	11.969651000	18.489853000	3.574078000
1	11.599718000	16.756510000	3.678659000
1	9.604390000	17.139094000	2.095408000
1	10.104531000	18.848487000	2.016013000
1	8.430259000	18.431109000	2.438517000
1	8.640830000	19.818370000	4.620119000
1	10.298758000	20.237065000	4.126223000
1	9.998663000	19.508192000	5.724937000

Energy = -5278.051650 A.U.

### 2.3.2 FeCl<sub>2</sub>(dpbz) optimized with uPBE/PBE/TZVP (toluene PCM)

26	2.479975000	7.459875000	3.755326000
17	1.656390000	9.162622000	2.549976000
17	1.238534000	6.184538000	5.089910000
15	3.994621000	6.275499000	2.299654000
15	4.549407000	8.230564000	4.721576000
6	5.466720000	7.403814000	2.193664000
6	6.300528000	7.443741000	1.067295000
1	6.093814000	6.786394000	0.220400000
6	7.375952000	8.333805000	1.013242000
1	8.015028000	8.359223000	0.128494000
6	7.622472000	9.198132000	2.083732000
1	8.455474000	9.902461000	2.040245000
6	6.793595000	9.173044000	3.208125000
1	6.973636000	9.866162000	4.032388000
6	5.715614000	8.278755000	3.276974000
6	3.596833000	5.890935000	0.533359000
6	4.005336000	4.703579000	-0.093738000
1	4.580981000	3.960312000	0.460743000
6	3.670708000	4.467340000	-1.430785000
1	3.990117000	3.540243000	-1.911221000
6	2.929286000	5.410633000	-2.147665000
1	2.668046000	5.222870000	-3.190991000
6	2.513479000	6.590998000	-1.522300000
1	1.923010000	7.325424000	-2.073596000
6	2.835877000	6.829857000	-0.184783000
1	2.488943000	7.741613000	0.308037000
6	4.652747000	4.688512000	2.979207000
6	6.016354000	4.358077000	2.952986000
1	6.743701000	5.059728000	2.540394000
6	6.449205000	3.130217000	3.461398000
1	7.512308000	2.881694000	3.440851000
6	5.526822000	2.225511000	3.995003000
1	5.867822000	1.267385000	4.392168000
6	4.167959000	2.553987000	4.027681000
1	3.444207000	1.856802000	4.454109000
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1	7.337800000	7.163561000	5.119038000
6	7.232359000	5.878811000	6.850673000
1	8.294786000	5.628996000	6.816215000
6	6.414381000	5.333326000	7.844415000
1	6.836911000	4.656059000	8.589305000
6	5.052681000	5.649282000	7.877368000
1	4.406756000	5.216403000	8.643603000

6	4.507192000	6.508456000	6.920833000
1	3.437420000	6.727977000	6.932081000
6	4.727968000	9.898281000	5.502904000
6	4.015956000	10.967363000	4.931295000
1	3.377619000	10.793772000	4.061300000
6	4.114348000	12.246278000	5.482969000
1	3.558712000	13.071396000	5.033069000
6	4.905504000	12.466402000	6.615678000
1	4.972914000	13.465695000	7.050260000
6	5.601276000	11.402124000	7.195779000
1	6.213799000	11.566384000	8.084698000
6	5.515357000	10.120342000	6.643296000
1	6.058954000	9.293659000	7.104123000

Energy = -4022.254510 A.U.

### 2.3.3 FeCl<sub>2</sub>(<sup>t</sup>Bu dppe) optimized with uPBE/PBE/TZVP (toluene PCM)

26	8.613986000	6.905554000	8.682715000
17	10.832528000	7.137466000	8.774611000
17	7.642200000	6.513431000	6.702745000
15	7.597772000	8.664264000	10.045668000
15	7.824612000	5.405310000	10.434155000
6	6.731389000	6.456864000	11.539482000
1	5.760572000	6.510970000	11.022121000
1	6.548663000	5.961525000	12.504815000
6	7.326410000	7.855516000	11.720461000
1	8.317507000	7.808861000	12.198189000
1	6.690163000	8.485426000	12.359520000
6	8.523119000	10.206460000	10.483329000
6	7.925802000	11.471864000	10.466500000
1	6.877808000	11.563438000	10.178138000
6	8.660452000	12.617423000	10.811297000
6	10.006332000	12.453108000	11.174203000
1	10.587053000	13.332404000	11.445509000
6	10.636931000	11.197420000	11.188951000
6	9.875744000	10.076300000	10.829117000
1	10.345341000	9.091008000	10.785544000
6	5.913778000	9.232101000	9.533292000
6	5.621747000	9.255246000	8.167215000
1	6.366731000	8.882604000	7.461475000
6	4.379667000	9.725646000	7.699854000
6	3.447733000	10.154486000	8.650966000
1	2.477829000	10.517023000	8.309660000
6	3.704901000	10.134726000	10.036520000
6	4.953586000	9.671531000	10.462901000
1	5.188378000	9.660617000	11.526672000
6	9.158475000	4.757891000	11.541030000
6	10.269236000	4.181193000	10.917861000
1	10.331925000	4.199160000	9.827921000
6	11.304611000	3.602702000	11.672086000
6	11.193337000	3.643472000	13.067327000
1	11.988486000	3.205707000	13.671550000
6	10.100433000	4.235754000	13.728239000
6	9.082067000	4.789308000	12.943439000
1	8.222360000	5.248420000	13.429016000
6	6.755272000	3.934471000	10.090053000
6	6.591338000	2.910518000	11.038457000
1	7.145669000	2.961718000	11.975577000
6	5.742861000	1.830804000	10.775476000
6	5.065748000	1.808664000	9.538946000
1	4.405403000	0.967042000	9.326524000
6	5.213751000	2.810594000	8.573696000
6	6.079967000	3.880475000	8.868923000

1	6.247668000	4.672444000	8.134938000
6	12.121427000	11.019285000	11.551640000
6	12.780616000	12.336836000	11.993449000
1	12.288927000	12.766573000	12.879750000
1	12.771247000	13.091335000	11.192417000
1	13.832492000	12.148227000	12.254935000
6	12.253131000	10.003601000	12.709056000
1	11.717645000	10.354385000	13.604491000
1	13.313442000	9.870208000	12.973999000
1	11.852104000	9.017504000	12.435292000
6	12.879335000	10.483881000	10.315404000
1	13.943737000	10.338398000	10.558421000
1	12.813036000	11.194977000	9.478269000
1	12.473730000	9.521517000	9.971690000
6	7.971052000	13.993344000	10.781122000
6	8.922662000	15.136415000	11.173359000
1	9.777553000	15.213150000	10.484772000
1	9.311278000	15.016041000	12.195887000
1	8.380118000	16.092865000	11.135288000
6	7.445208000	14.271135000	9.354911000
1	8.270054000	14.277857000	8.626895000
1	6.947392000	15.252770000	9.319100000
1	6.717517000	13.512463000	9.033079000
6	6.783749000	13.992047000	11.770546000
1	7.128026000	13.797676000	12.797611000
1	6.040151000	13.224342000	11.511010000
1	6.277572000	14.969973000	11.757456000
6	4.091330000	9.732982000	6.189663000
6	2.722709000	10.350570000	5.858214000
1	1.894360000	9.780059000	6.305132000
1	2.574690000	10.346089000	4.768209000
1	2.649145000	11.394922000	6.198577000
6	5.181408000	10.551516000	5.461684000
1	6.182605000	10.124123000	5.611533000
1	5.197582000	11.592749000	5.817893000
1	4.981938000	10.562398000	4.379049000
6	4.111905000	8.278711000	5.666094000
1	3.339728000	7.672053000	6.163627000
1	5.085154000	7.796098000	5.835549000
1	3.911480000	8.266309000	4.583333000
6	2.622733000	10.620018000	11.016850000
6	3.075144000	10.524200000	12.483808000
1	3.959150000	11.148959000	12.682756000
1	3.308134000	9.488534000	12.774478000
1	2.266251000	10.877837000	13.140101000
6	2.279400000	12.096009000	10.712964000
1	3.163620000	12.739504000	10.836726000
1	1.497953000	12.452556000	11.401858000

1	1.906958000	12.226191000	9.686866000
6	1.353450000	9.755419000	10.844680000
1	1.567014000	8.696689000	11.054679000
1	0.949456000	9.822029000	9.824435000
1	0.568705000	10.092061000	11.539794000
6	4.487293000	2.778340000	7.219038000
6	3.605102000	4.040131000	7.084671000
1	4.202724000	4.960926000	7.140890000
1	2.845495000	4.075567000	7.880475000
1	3.085510000	4.035835000	6.113811000
6	3.589480000	1.539678000	7.065102000
1	4.167470000	0.604436000	7.116860000
1	3.093748000	1.567958000	6.083436000
1	2.802374000	1.504245000	7.833807000
6	5.534012000	2.767439000	6.081455000
1	6.182433000	1.881163000	6.152902000
1	6.174073000	3.660743000	6.106304000
1	5.027320000	2.743202000	5.103941000
6	5.533355000	0.679685000	11.774058000
6	5.974360000	-0.649635000	11.120783000
1	5.397197000	-0.869150000	10.211077000
1	5.826577000	-1.485147000	11.822725000
1	7.039098000	-0.616873000	10.845411000
6	4.037170000	0.592751000	12.150645000
1	3.403042000	0.417220000	11.269831000
1	3.698555000	1.523324000	12.630638000
1	3.870821000	-0.236954000	12.855280000
6	6.344510000	0.871330000	13.066626000
1	7.426588000	0.909364000	12.870381000
1	6.158779000	0.024855000	13.744408000
1	6.056637000	1.791168000	13.598199000
6	10.061407000	4.252942000	15.266339000
6	11.289669000	5.026059000	15.797554000
1	11.278408000	5.048483000	16.898404000
1	11.286591000	6.064340000	15.432916000
1	12.233260000	4.560202000	15.479913000
6	8.794225000	4.931438000	15.814046000
1	7.878770000	4.407332000	15.499561000
1	8.721093000	5.982242000	15.495243000
1	8.819462000	4.920495000	16.913778000
6	10.098740000	2.801820000	15.796741000
1	9.230960000	2.229246000	15.435315000
1	10.077325000	2.799494000	16.897615000
1	11.008147000	2.273132000	15.477238000
6	12.515802000	2.987524000	10.951022000
6	13.275876000	4.110028000	10.208978000
1	12.631416000	4.632905000	9.488494000
1	14.132841000	3.687754000	9.661097000

1	13.657948000	4.858246000	10.919737000
6	12.031155000	1.934655000	9.929479000
1	11.380702000	2.375923000	9.161360000
1	11.470325000	1.129460000	10.427888000
1	12.894104000	1.484155000	9.415599000
6	13.489453000	2.298580000	11.922248000
1	13.921981000	3.005985000	12.645951000
1	14.323522000	1.862889000	11.352507000
1	13.004550000	1.482749000	12.480140000

Energy = -5125.787596 A.U.

### 2.3.4 FeCl<sub>2</sub>(Xantphos) optimized with uPBE/PBE/TZVP (gas phase calculation)

26	5.559365000	3.569867000	4.082921000
17	6.572323000	3.556117000	2.097988000
17	5.535374000	1.976636000	5.644631000
15	6.464057000	5.525131000	5.239168000
15	3.199254000	3.965957000	3.592537000
8	3.635057000	5.561615000	6.009126000
6	5.797532000	5.808081000	6.945597000
6	6.608188000	5.985406000	8.075109000
1	7.691823000	6.028165000	7.958485000
6	6.036012000	6.077533000	9.345141000
1	6.677027000	6.205918000	10.219005000
6	4.650384000	5.994774000	9.506182000
1	4.226034000	6.062301000	10.508607000
6	0.638376000	4.046578000	7.484065000
1	0.064028000	4.037629000	8.411125000
6	0.216352000	3.256235000	6.411633000
1	-0.678086000	2.638980000	6.511621000
6	0.936389000	3.242882000	5.215558000
1	0.613833000	2.608266000	4.389104000
6	2.094067000	4.020537000	5.079437000
6	2.274222000	5.810976000	8.469039000
6	1.752918000	7.236020000	8.129924000
1	2.095141000	7.562959000	7.138197000
1	2.115868000	7.959229000	8.875649000
1	0.652636000	7.247615000	8.135403000
6	1.763536000	5.417352000	9.861622000
1	2.106058000	4.414505000	10.153922000
1	0.665347000	5.433444000	9.890430000
1	2.105184000	6.137731000	10.617675000
6	4.409686000	5.738885000	7.141847000
6	3.804647000	5.832349000	8.402273000
6	1.780235000	4.850484000	7.382264000
6	2.485319000	4.808886000	6.172442000
6	8.287358000	5.362850000	5.536549000
6	9.158291000	6.462912000	5.519675000
1	8.769718000	7.462784000	5.317870000
6	10.524343000	6.279452000	5.751388000
1	11.196483000	7.139944000	5.731681000
6	11.028733000	5.000087000	6.002025000
1	12.096931000	4.858404000	6.178789000
6	10.164259000	3.901462000	6.017655000
1	10.553743000	2.898729000	6.204216000
6	8.799364000	4.077397000	5.779068000
1	8.127851000	3.214673000	5.781461000
6	6.318552000	7.171552000	4.405795000
6	5.871483000	8.322317000	5.070770000

1	5.592127000	8.270078000	6.124733000
6	5.789741000	9.540439000	4.389324000
1	5.439170000	10.430916000	4.915490000
6	6.160568000	9.620006000	3.044781000
1	6.100163000	10.573076000	2.515419000
6	6.607223000	8.474036000	2.378945000
1	6.894218000	8.527968000	1.326725000
6	6.678436000	7.252033000	3.049531000
1	7.009756000	6.355392000	2.519221000
6	2.749839000	5.483834000	2.633948000
6	1.668486000	6.304251000	2.986165000
1	1.058722000	6.057547000	3.857198000
6	1.365711000	7.434718000	2.221651000
1	0.522977000	8.068909000	2.505102000
6	2.134226000	7.748932000	1.098036000
1	1.894898000	8.630637000	0.500040000
6	3.213283000	6.932716000	0.744208000
1	3.822018000	7.176588000	-0.128885000
6	3.528981000	5.809532000	1.510919000
1	4.385275000	5.184997000	1.242727000
6	2.465504000	2.588961000	2.592151000
6	1.509807000	2.803497000	1.587559000
1	1.168837000	3.816196000	1.364825000
6	0.998444000	1.722197000	0.864056000
1	0.258760000	1.898199000	0.080135000
6	1.433850000	0.422997000	1.139460000
1	1.035061000	-0.419589000	0.570841000
6	2.387308000	0.205703000	2.138913000
1	2.738313000	-0.805778000	2.352643000
6	2.909189000	1.282616000	2.858500000
1	3.663808000	1.110288000	3.630615000

Energy = -4444.728015 A.U.

### 2.3.5 FeCl(dppe)<sub>2</sub> optimized with uPBE/PBE/TZVP (toluene PCM)

26	2.737266000	17.791530000	5.350174000
17	2.876994000	17.807051000	3.011086000
15	1.293058000	16.641329000	6.609276000
15	3.902314000	15.859706000	5.439797000
15	1.577824000	19.723811000	5.305749000
15	4.012482000	18.940111000	6.789346000
6	2.189522000	15.263597000	7.586594000
1	2.128480000	15.482502000	8.660097000
1	1.624955000	14.336639000	7.415625000
6	3.651270000	15.126291000	7.146102000
1	3.989763000	14.081243000	7.188162000
1	4.306481000	15.717128000	7.800019000
6	0.048789000	15.583426000	5.674981000
6	0.154646000	15.490560000	4.281871000
1	0.934302000	16.060259000	3.767825000
6	-0.708761000	14.662118000	3.556412000
1	-0.609042000	14.597590000	2.470700000
6	-1.685170000	13.914848000	4.218908000
1	-2.359850000	13.267632000	3.654251000
6	-1.792776000	13.994226000	5.612673000
1	-2.552525000	13.410675000	6.137816000
6	-0.930870000	14.822076000	6.336024000
1	-1.030534000	14.881204000	7.422579000
6	0.159771000	17.364999000	7.912420000
6	0.582932000	17.557687000	9.238811000
1	1.567634000	17.212421000	9.556927000
6	-0.243456000	18.181855000	10.178204000
1	0.106338000	18.309323000	11.205148000
6	-1.513259000	18.633806000	9.807113000
1	-2.161163000	19.119460000	10.539389000
6	-1.945345000	18.454363000	8.489593000
1	-2.934352000	18.802614000	8.184186000
6	-1.119373000	17.828555000	7.552182000
1	-1.478324000	17.697359000	6.530286000
6	3.469878000	14.441606000	4.296074000
6	2.841143000	13.273503000	4.754299000
1	2.570137000	13.161453000	5.804638000
6	2.543392000	12.228429000	3.873877000
1	2.054553000	11.328185000	4.252506000
6	2.866867000	12.336767000	2.519705000
1	2.635935000	11.520699000	1.831844000
6	3.489792000	13.498434000	2.052133000
1	3.746733000	13.595237000	0.995009000
6	3.789244000	14.542016000	2.930298000
1	4.263418000	15.446655000	2.550037000
6	5.750374000	15.830569000	5.200219000

6	6.581064000	14.934667000	5.892231000
1	6.161567000	14.239969000	6.621611000
6	7.958519000	14.923280000	5.656501000
1	8.595105000	14.226371000	6.206200000
6	8.519808000	15.796714000	4.719195000
1	9.596197000	15.785343000	4.535587000
6	7.696012000	16.679875000	4.015367000
1	8.125232000	17.362884000	3.279269000
6	6.318920000	16.698255000	4.255699000
1	5.674790000	17.388528000	3.708234000
6	1.602688000	20.461017000	7.027348000
1	1.316089000	21.521855000	7.007275000
1	0.822088000	19.917182000	7.575766000
6	2.969494000	20.259624000	7.696373000
1	2.836761000	19.945017000	8.738809000
1	3.557185000	21.187827000	7.711691000
6	-0.224597000	19.765377000	4.831132000
6	-1.122201000	20.686933000	5.394275000
1	-0.785801000	21.397329000	6.151295000
6	-2.461025000	20.704504000	4.994361000
1	-3.150310000	21.421512000	5.445980000
6	-2.916596000	19.811359000	4.018797000
1	-3.963057000	19.826999000	3.707182000
6	-2.024433000	18.903080000	3.442345000
1	-2.369576000	18.203473000	2.678147000
6	-0.686194000	18.878854000	3.847056000
1	0.008364000	18.166692000	3.398377000
6	2.162097000	21.143797000	4.233107000
6	2.789396000	22.277150000	4.773174000
1	2.965158000	22.358960000	5.846468000
6	3.212412000	23.323189000	3.947044000
1	3.698111000	24.195797000	4.389076000
6	3.018291000	23.249733000	2.566035000
1	3.347177000	24.066446000	1.920032000
6	2.398835000	22.122212000	2.017192000
1	2.242786000	22.053253000	0.938406000
6	1.973935000	21.078000000	2.841371000
1	1.501681000	20.200857000	2.399211000
6	5.330241000	20.041973000	6.022570000
6	5.449102000	20.089491000	4.628504000
1	4.783922000	19.476202000	4.014324000
6	6.388632000	20.930989000	4.022868000
1	6.464538000	20.959468000	2.933741000
6	7.215902000	21.738269000	4.806549000
1	7.949145000	22.396323000	4.335183000
6	7.098405000	21.704703000	6.201521000
1	7.740915000	22.334463000	6.821294000
6	6.162213000	20.862099000	6.805118000

1	6.089702000	20.836048000	7.895313000
6	5.015064000	18.224437000	8.200218000
6	6.346969000	17.829135000	7.979819000
1	6.810008000	18.009609000	7.008917000
6	7.090124000	17.214913000	8.991143000
1	8.123022000	16.920026000	8.794162000
6	6.518860000	16.978663000	10.245289000
1	7.101442000	16.502119000	11.036162000
6	5.194472000	17.360934000	10.477318000
1	4.735933000	17.187122000	11.453411000
6	4.451205000	17.972655000	9.463256000
1	3.419727000	18.258898000	9.673140000

Energy = -5096.171316 A.U.

### 2.3.6 FeCl(dpbz)<sub>2</sub> optimized with uPBE/PBE/TZVP (toluene PCM)

26	5.064192000	2.433568000	6.643351000
15	3.478121000	1.226898000	5.593272000
17	5.177854000	2.684415000	8.955273000
6	7.363803000	1.786741000	4.301397000
6	7.931249000	1.777911000	3.019813000
1	7.848562000	2.660550000	2.382210000
6	8.591224000	0.636639000	2.552675000
1	9.018638000	0.629053000	1.547654000
6	8.709416000	-0.488285000	3.374167000
1	9.227846000	-1.379060000	3.013379000
6	8.158172000	-0.478959000	4.659337000
1	8.253112000	-1.363910000	5.290268000
6	7.466220000	0.648063000	5.120100000
6	7.895476000	4.255955000	5.699961000
6	7.622631000	5.300764000	6.597630000
1	6.597110000	5.488381000	6.918380000
6	8.654603000	6.100625000	7.094703000
1	8.419563000	6.912714000	7.786227000
6	9.979221000	5.855786000	6.718378000
1	10.787376000	6.474778000	7.113726000
6	10.262259000	4.806695000	5.839488000
1	11.294121000	4.598610000	5.547911000
6	9.228357000	4.014406000	5.330492000
1	9.468253000	3.200317000	4.645208000
15	6.453436000	3.236343000	5.059664000
15	6.673881000	0.852844000	6.796679000
6	6.049440000	4.218673000	3.507096000
6	4.966586000	3.820038000	2.706372000
1	4.352648000	2.970625000	3.005361000
6	4.644178000	4.514224000	1.537416000
1	3.796917000	4.184707000	0.932262000
6	5.394713000	5.629917000	1.152375000
1	5.140066000	6.177377000	0.242500000
6	6.471951000	6.038310000	1.942987000
1	7.066424000	6.907815000	1.653410000
6	6.798770000	5.337962000	3.109012000
1	7.642134000	5.673396000	3.713064000
15	3.473480000	4.040623000	6.559594000
6	8.209155000	1.129496000	7.845033000
6	8.439728000	2.354387000	8.482412000
1	7.686840000	3.137864000	8.425487000
6	9.615405000	2.561995000	9.211910000
1	9.776173000	3.522298000	9.706401000
6	10.574504000	1.552023000	9.309087000
1	11.491141000	1.715994000	9.879817000
6	10.351358000	0.324361000	8.675823000

1	11.091480000	-0.475502000	8.749437000
6	9.176492000	0.114680000	7.951133000
1	9.011038000	-0.855908000	7.480150000
6	6.230243000	-0.861607000	7.364431000
6	6.208273000	-1.114693000	8.748786000
1	6.511532000	-0.332093000	9.446881000
6	5.800121000	-2.358827000	9.233921000
1	5.790685000	-2.540492000	10.310716000
6	5.407339000	-3.366987000	8.346632000
1	5.092115000	-4.340884000	8.726627000
6	5.416734000	-3.118642000	6.971726000
1	5.105982000	-3.896212000	6.270684000
6	5.818198000	-1.871732000	6.481424000
1	5.802043000	-1.689447000	5.406711000
6	2.405942000	3.740701000	5.058749000
6	1.604588000	4.691007000	4.413274000
1	1.589455000	5.725834000	4.758793000
6	0.831687000	4.324578000	3.307109000
1	0.226149000	5.076002000	2.796108000
6	0.838948000	3.001803000	2.854847000
1	0.237839000	2.714680000	1.989359000
6	1.610465000	2.041023000	3.516271000
1	1.608672000	1.005925000	3.168790000
6	2.397469000	2.404974000	4.617657000
6	3.999459000	5.824007000	6.489450000
6	4.300713000	6.457703000	7.710535000
1	4.155013000	5.920551000	8.650034000
6	4.785499000	7.766485000	7.728786000
1	5.011259000	8.244363000	8.684447000
6	4.981027000	8.461971000	6.529983000
1	5.357602000	9.486720000	6.544419000
6	4.694823000	7.835473000	5.314666000
1	4.850318000	8.366399000	4.373123000
6	2.119941000	4.189558000	7.858259000
6	1.909989000	3.180910000	8.806322000
1	2.591881000	2.334227000	8.849115000
6	0.849388000	3.273264000	9.714614000
1	0.705427000	2.479937000	10.451105000
6	-0.014919000	4.369303000	9.682997000
1	-0.841368000	4.439965000	10.393527000
6	0.187857000	5.381309000	8.738377000
1	-0.478235000	6.246420000	8.707162000
6	1.247969000	5.292117000	7.834142000
1	1.402951000	6.099731000	7.116720000
6	4.212410000	6.522180000	5.291180000
1	4.011085000	6.044660000	4.332092000
6	2.212018000	0.444071000	6.738344000
6	2.684073000	-0.230861000	7.875463000

1	3.755154000	-0.267211000	8.078084000
6	1.793179000	-0.839846000	8.763067000
1	2.181313000	-1.364316000	9.638903000
6	0.414873000	-0.765770000	8.538420000
1	-0.282654000	-1.232425000	9.237253000
6	-0.064786000	-0.081836000	7.417801000
1	-1.139778000	-0.008077000	7.238790000
6	0.826722000	0.515722000	6.521153000
1	0.433997000	1.046287000	5.652700000
6	3.665268000	-0.161887000	4.340178000
6	4.550025000	0.010702000	3.263192000
1	5.132490000	0.927671000	3.180744000
6	4.712363000	-0.987510000	2.299858000
1	5.406643000	-0.829207000	1.471861000
6	3.998931000	-2.186284000	2.403074000
1	4.128833000	-2.970460000	1.654333000
6	3.119895000	-2.372229000	3.473273000
1	2.556718000	-3.303735000	3.564902000
6	2.952109000	-1.368495000	4.433659000
1	2.262734000	-1.530670000	5.262916000

Energy = -5400.697242 A.U.

### 3. X-Ray Crystallographic Data

#### 3.1 ${}^{\text{tB}}\text{u}\text{dppe}$

REFERENCE NUMBER: neijk01

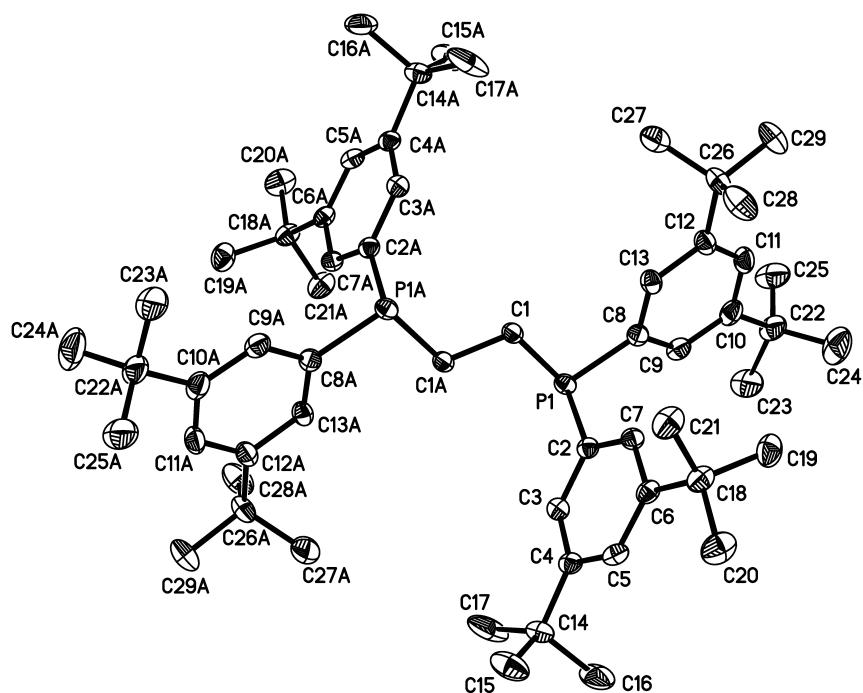
#### CRYSTAL STRUCTURE REPORT



Report prepared for:

J. Kneebone, Prof. M. Neidig

November 30, 2012



William W. Brennessel  
X-ray Crystallographic Facility  
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120 Trustee Road  
Rochester, NY 14627

#### Data collection

A crystal ( $0.38 \times 0.30 \times 0.12 \text{ mm}^3$ ) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at  $100.0(5) \text{ K}$ .<sup>1</sup> A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 4.03 cm. A randomly oriented region of reciprocal space was surveyed: five major sections of frames were collected with  $0.50^\circ$  steps in  $\omega$  at five different  $\phi$  settings and a detector position of  $-38^\circ$  in  $2\theta$ . The intensity data were corrected for absorption.<sup>2</sup> Final cell constants were calculated from the xyz centroids of 3989 strong reflections from the actual data collection after integration.<sup>3</sup> See Table 1 for additional crystal and refinement information.

#### Structure solution and refinement

The structure was solved using SIR97<sup>4</sup> and refined using SHELXL-2012.<sup>5</sup> The space group  $P2_1/c$  was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to  $R1 = 0.0512 (F^2, I > 2\sigma(I))$  and  $wR2 = 0.1270 (F^2, \text{all data})$ .

#### Structure description

The structure is the one suggested. The molecule lies in a crystallographic inversion center; thus, one-half is unique. Four (two unique) *tert*-butyl groups are modeled as rotationally disordered over two positions each (70:30 and 59:41, for groups originating at atoms C14 and C22, respectively).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

<sup>1</sup> APEX2, version 2012.4-3; Bruker AXS: Madison, WI, 2012.

<sup>2</sup> Sheldrick, G. M. SADABS, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

<sup>3</sup> SAINT, version 7.68A; Bruker AXS: Madison, WI, 2009.

<sup>4</sup> Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: A new program for solving and refining crystal structures; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

<sup>5</sup> Sheldrick, G. M. SHELXL-2012 University of Göttingen: Göttingen, Germany, 2012.

Some equations of interest:

$$R_{\text{int}} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R1 = \sum ||F_o|| - |F_c|| / \sum |F_o|$$

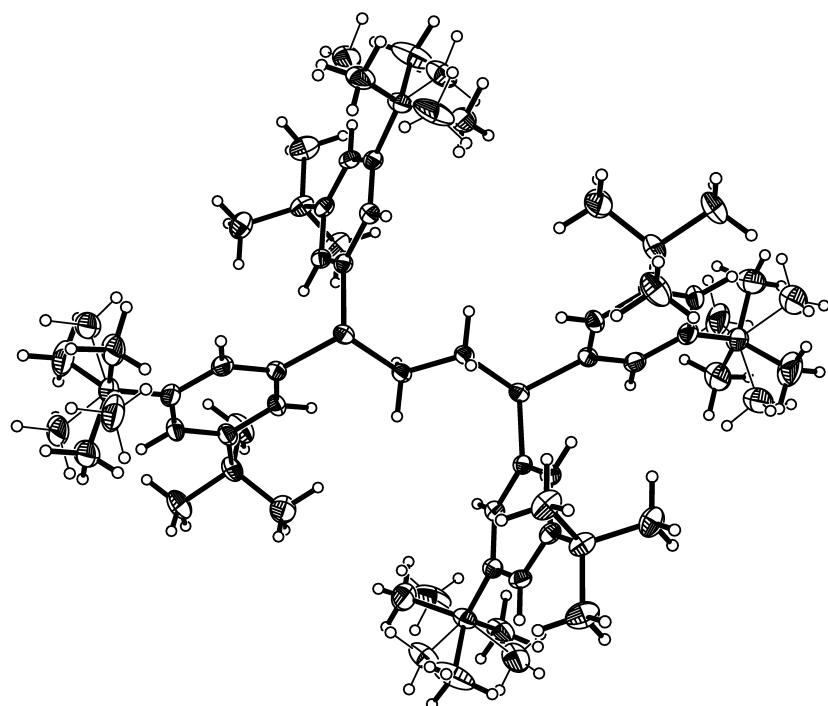
$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

where  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\sum [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where  $m$  = number of reflections and  $n$  = number of parameters



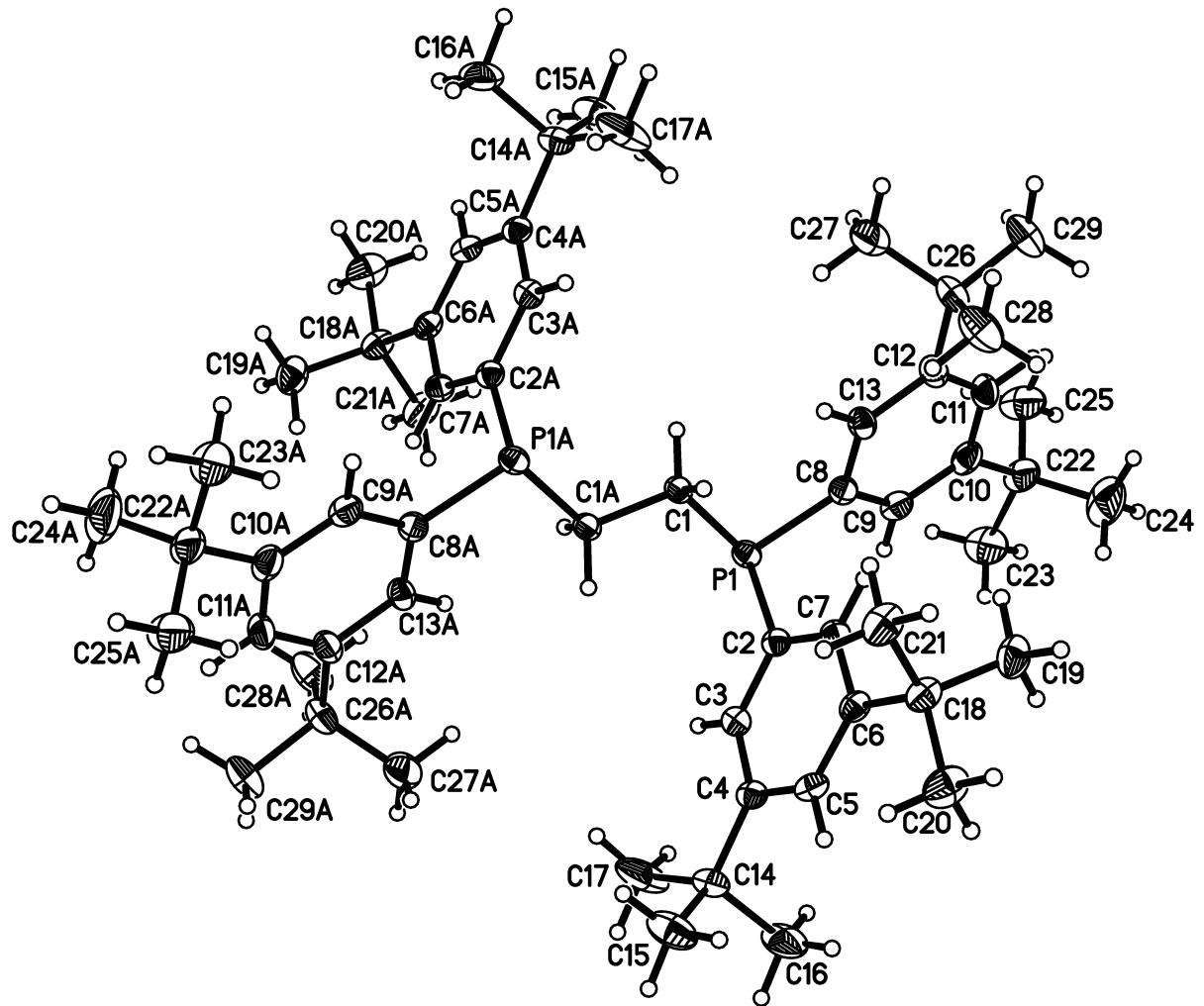


Table S1. Crystal data and structure refinement for neijk01.

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Identification code	neijk01	
Empirical formula	C58 H88 P2	
Formula weight	847.22	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	
Unit cell dimensions	<i>a</i> = 14.6204(15) Å	$\alpha$ = 90°
	<i>b</i> = 18.6371(19) Å	$\beta$ = 97.648(2)°
	<i>c</i> = 10.1420(10) Å	$\gamma$ = 90°
Volume	2738.9(5) Å <sup>3</sup>	
<i>Z</i>	2	
Density (calculated)	1.027 Mg/m <sup>3</sup>	
Absorption coefficient	0.113 mm <sup>-1</sup>	
<i>F</i> (000)	932	
Crystal color, morphology	colorless, plate	
Crystal size	0.38 x 0.30 x 0.12 mm <sup>3</sup>	
Theta range for data collection	1.780 to 30.508°	
Index ranges	-20 ≤ <i>h</i> ≤ 20, -26 ≤ <i>k</i> ≤ 26, -14 ≤ <i>l</i> ≤ 14	
Reflections collected	50173	
Independent reflections	8357 [ <i>R</i> (int) = 0.0953]	
Observed reflections	5438	
Completeness to theta = 30.510°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7461 and 0.6420	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameters	8357 / 18 / 345	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.023	
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> 1 = 0.0512, <i>wR</i> 2 = 0.1080	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0943, <i>wR</i> 2 = 0.1270	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.344 and -0.301 e.Å <sup>-3</sup>	

Table S2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk01.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
P1	9308(1)	289(1)	2971(1)	20(1)
C1	9527(1)	-115(1)	4649(1)	19(1)
C2	8916(1)	1178(1)	3424(1)	19(1)
C3	9524(1)	1751(1)	3371(1)	20(1)
C4	9299(1)	2438(1)	3749(1)	20(1)
C5	8442(1)	2537(1)	4179(1)	22(1)
C6	7815(1)	1983(1)	4242(1)	21(1)
C7	8066(1)	1301(1)	3851(1)	20(1)
C8	8228(1)	-155(1)	2303(1)	21(1)
C9	7978(1)	-141(1)	924(2)	25(1)
C10	7201(1)	-502(1)	325(2)	28(1)
C11	6680(1)	-889(1)	1134(2)	28(1)
C12	6909(1)	-918(1)	2510(2)	24(1)
C13	7686(1)	-541(1)	3072(2)	22(1)
C14	9945(1)	3075(1)	3638(2)	26(1)
C15	10042(3)	3527(2)	4887(4)	42(1)
C16	9497(3)	3547(2)	2463(3)	50(1)
C17	10902(2)	2860(2)	3345(5)	53(1)
C15'	9679(9)	3745(5)	4398(12)	56(3)
C16'	9989(7)	3245(4)	2242(6)	39(2)
C17'	10925(6)	2850(4)	4328(13)	58(3)
C18	6880(1)	2084(1)	4745(2)	26(1)
C19	6106(1)	1806(1)	3701(2)	33(1)
C20	6682(1)	2870(1)	5022(2)	37(1)
C21	6881(1)	1655(1)	6035(2)	33(1)
C22	6925(1)	-488(1)	-1191(2)	36(1)
C23	7662(3)	-59(2)	-1932(3)	49(1)
C24	6023(3)	-111(2)	-1557(4)	57(1)
C25	6924(3)	-1242(2)	-1735(3)	51(1)
C23'	6007(4)	-972(3)	-1607(4)	46(2)
C24'	7663(4)	-779(4)	-1861(4)	54(2)

C25'	6638(4)	264(3)	-1551(5)	44(1)
C26	6345(1)	-1336(1)	3421(2)	30(1)
C27	6982(1)	-1824(1)	4348(2)	44(1)
C28	5869(1)	-797(1)	4248(2)	42(1)
C29	5607(1)	-1809(1)	2643(2)	40(1)

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Table S3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for neijk01.

P(1)-C(8)	1.8308(15)	C(15)-H(15A)	0.9800
P(1)-C(2)	1.8327(15)	C(15)-H(15B)	0.9800
P(1)-C(1)	1.8491(15)	C(15)-H(15C)	0.9800
C(1)-C(1)#1	1.529(3)	C(16)-H(16A)	0.9800
C(1)-H(1A)	0.9900	C(16)-H(16B)	0.9800
C(1)-H(1B)	0.9900	C(16)-H(16C)	0.9800
C(2)-C(7)	1.3878(19)	C(17)-H(17A)	0.9800
C(2)-C(3)	1.395(2)	C(17)-H(17B)	0.9800
C(3)-C(4)	1.390(2)	C(17)-H(17C)	0.9800
C(3)-H(3)	0.9500	C(15')-H(15D)	0.9800
C(4)-C(5)	1.392(2)	C(15')-H(15E)	0.9800
C(4)-C(14)	1.529(2)	C(15')-H(15F)	0.9800
C(5)-C(6)	1.389(2)	C(16')-H(16D)	0.9800
C(5)-H(5)	0.9500	C(16')-H(16E)	0.9800
C(6)-C(7)	1.395(2)	C(16')-H(16F)	0.9800
C(6)-C(18)	1.533(2)	C(17')-H(17D)	0.9800
C(7)-H(7)	0.9500	C(17')-H(17E)	0.9800
C(8)-C(13)	1.385(2)	C(17')-H(17F)	0.9800
C(8)-C(9)	1.398(2)	C(18)-C(20)	1.526(2)
C(9)-C(10)	1.388(2)	C(18)-C(19)	1.533(2)
C(9)-H(9)	0.9500	C(18)-C(21)	1.533(2)
C(10)-C(11)	1.393(2)	C(19)-H(19A)	0.9800
C(10)-C(22)	1.537(2)	C(19)-H(19B)	0.9800
C(11)-C(12)	1.392(2)	C(19)-H(19C)	0.9800
C(11)-H(11)	0.9500	C(20)-H(20A)	0.9800
C(12)-C(13)	1.392(2)	C(20)-H(20B)	0.9800
C(12)-C(26)	1.531(2)	C(20)-H(20C)	0.9800
C(13)-H(13)	0.9500	C(21)-H(21A)	0.9800
C(14)-C(16')	1.461(6)	C(21)-H(21B)	0.9800
C(14)-C(15)	1.513(4)	C(21)-H(21C)	0.9800
C(14)-C(17)	1.522(3)	C(22)-C(24')	1.455(5)
C(14)-C(15')	1.544(9)	C(22)-C(25')	1.494(5)
C(14)-C(16)	1.554(4)	C(22)-C(24)	1.496(4)
C(14)-C(17')	1.566(7)	C(22)-C(25)	1.511(4)

C(22)-C(23)	1.607(4)	C(1)#1-C(1)-H(1A)	109.6
C(22)-C(23')	1.625(5)	P(1)-C(1)-H(1A)	109.6
C(23)-H(23A)	0.9800	C(1)#1-C(1)-H(1B)	109.6
C(23)-H(23B)	0.9800	P(1)-C(1)-H(1B)	109.6
C(23)-H(23C)	0.9800	H(1A)-C(1)-H(1B)	108.1
C(24)-H(24A)	0.9800	C(7)-C(2)-C(3)	119.25(13)
C(24)-H(24B)	0.9800	C(7)-C(2)-P(1)	123.39(11)
C(24)-H(24C)	0.9800	C(3)-C(2)-P(1)	117.33(11)
C(25)-H(25A)	0.9800	C(4)-C(3)-C(2)	121.26(13)
C(25)-H(25B)	0.9800	C(4)-C(3)-H(3)	119.4
C(25)-H(25C)	0.9800	C(2)-C(3)-H(3)	119.4
C(23')-H(23D)	0.9800	C(3)-C(4)-C(5)	117.65(13)
C(23')-H(23E)	0.9800	C(3)-C(4)-C(14)	121.60(13)
C(23')-H(23F)	0.9800	C(5)-C(4)-C(14)	120.70(13)
C(24')-H(24D)	0.9800	C(6)-C(5)-C(4)	122.93(14)
C(24')-H(24E)	0.9800	C(6)-C(5)-H(5)	118.5
C(24')-H(24F)	0.9800	C(4)-C(5)-H(5)	118.5
C(25')-H(25D)	0.9800	C(5)-C(6)-C(7)	117.67(13)
C(25')-H(25E)	0.9800	C(5)-C(6)-C(18)	123.17(13)
C(25')-H(25F)	0.9800	C(7)-C(6)-C(18)	119.15(13)
C(26)-C(29)	1.529(2)	C(2)-C(7)-C(6)	121.25(13)
C(26)-C(27)	1.532(3)	C(2)-C(7)-H(7)	119.4
C(26)-C(28)	1.534(2)	C(6)-C(7)-H(7)	119.4
C(27)-H(27A)	0.9800	C(13)-C(8)-C(9)	118.63(14)
C(27)-H(27B)	0.9800	C(13)-C(8)-P(1)	123.81(11)
C(27)-H(27C)	0.9800	C(9)-C(8)-P(1)	117.41(12)
C(28)-H(28A)	0.9800	C(10)-C(9)-C(8)	121.28(15)
C(28)-H(28B)	0.9800	C(10)-C(9)-H(9)	119.4
C(28)-H(28C)	0.9800	C(8)-C(9)-H(9)	119.4
C(29)-H(29A)	0.9800	C(9)-C(10)-C(11)	118.22(14)
C(29)-H(29B)	0.9800	C(9)-C(10)-C(22)	121.32(16)
C(29)-H(29C)	0.9800	C(11)-C(10)-C(22)	120.46(15)
C(8)-P(1)-C(2)	102.59(6)	C(12)-C(11)-C(10)	122.20(14)
C(8)-P(1)-C(1)	101.06(7)	C(12)-C(11)-H(11)	118.9
C(2)-P(1)-C(1)	99.14(6)	C(10)-C(11)-H(11)	118.9
C(1)#1-C(1)-P(1)	110.48(13)	C(11)-C(12)-C(13)	117.74(15)

C(11)-C(12)-C(26)	123.22(14)	C(14)-C(15')-H(15E)	109.5
C(13)-C(12)-C(26)	119.03(13)	H(15D)-C(15')-H(15E)	109.5
C(8)-C(13)-C(12)	121.93(14)	C(14)-C(15')-H(15F)	109.5
C(8)-C(13)-H(13)	119.0	H(15D)-C(15')-H(15F)	109.5
C(12)-C(13)-H(13)	119.0	H(15E)-C(15')-H(15F)	109.5
C(15)-C(14)-C(17)	108.9(2)	C(14)-C(16')-H(16D)	109.5
C(16')-C(14)-C(4)	110.3(3)	C(14)-C(16')-H(16E)	109.5
C(15)-C(14)-C(4)	111.15(19)	H(16D)-C(16')-H(16E)	109.5
C(17)-C(14)-C(4)	113.75(16)	C(14)-C(16')-H(16F)	109.5
C(16')-C(14)-C(15')	110.8(5)	H(16D)-C(16')-H(16F)	109.5
C(4)-C(14)-C(15')	113.1(4)	H(16E)-C(16')-H(16F)	109.5
C(15)-C(14)-C(16)	108.0(2)	C(14)-C(17')-H(17D)	109.5
C(17)-C(14)-C(16)	107.7(2)	C(14)-C(17')-H(17E)	109.5
C(4)-C(14)-C(16)	107.15(16)	H(17D)-C(17')-H(17E)	109.5
C(16')-C(14)-C(17')	109.6(5)	C(14)-C(17')-H(17F)	109.5
C(4)-C(14)-C(17')	107.2(3)	H(17D)-C(17')-H(17F)	109.5
C(15')-C(14)-C(17')	105.7(6)	H(17E)-C(17')-H(17F)	109.5
C(14)-C(15)-H(15A)	109.5	C(20)-C(18)-C(19)	108.12(14)
C(14)-C(15)-H(15B)	109.5	C(20)-C(18)-C(6)	112.26(13)
H(15A)-C(15)-H(15B)	109.5	C(19)-C(18)-C(6)	109.71(13)
C(14)-C(15)-H(15C)	109.5	C(20)-C(18)-C(21)	108.82(14)
H(15A)-C(15)-H(15C)	109.5	C(19)-C(18)-C(21)	109.26(14)
H(15B)-C(15)-H(15C)	109.5	C(6)-C(18)-C(21)	108.63(12)
C(14)-C(16)-H(16A)	109.5	C(18)-C(19)-H(19A)	109.5
C(14)-C(16)-H(16B)	109.5	C(18)-C(19)-H(19B)	109.5
H(16A)-C(16)-H(16B)	109.5	H(19A)-C(19)-H(19B)	109.5
C(14)-C(16)-H(16C)	109.5	C(18)-C(19)-H(19C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(16B)-C(16)-H(16C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(14)-C(17)-H(17A)	109.5	C(18)-C(20)-H(20A)	109.5
C(14)-C(17)-H(17B)	109.5	C(18)-C(20)-H(20B)	109.5
H(17A)-C(17)-H(17B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(14)-C(17)-H(17C)	109.5	C(18)-C(20)-H(20C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(17B)-C(17)-H(17C)	109.5	H(20B)-C(20)-H(20C)	109.5
C(14)-C(15')-H(15D)	109.5	C(18)-C(21)-H(21A)	109.5

C(18)-C(21)-H(21B)	109.5	C(22)-C(23')-H(23E)	109.5
H(21A)-C(21)-H(21B)	109.5	H(23D)-C(23')-H(23E)	109.5
C(18)-C(21)-H(21C)	109.5	C(22)-C(23')-H(23F)	109.5
H(21A)-C(21)-H(21C)	109.5	H(23D)-C(23')-H(23F)	109.5
H(21B)-C(21)-H(21C)	109.5	H(23E)-C(23')-H(23F)	109.5
C(24')-C(22)-C(25')	116.0(4)	C(22)-C(24')-H(24D)	109.5
C(24)-C(22)-C(25)	112.8(3)	C(22)-C(24')-H(24E)	109.5
C(24')-C(22)-C(10)	110.4(2)	H(24D)-C(24')-H(24E)	109.5
C(25')-C(22)-C(10)	106.8(2)	C(22)-C(24')-H(24F)	109.5
C(24)-C(22)-C(10)	111.2(2)	H(24D)-C(24')-H(24F)	109.5
C(25)-C(22)-C(10)	109.62(17)	H(24E)-C(24')-H(24F)	109.5
C(24)-C(22)-C(23)	106.0(2)	C(22)-C(25')-H(25D)	109.5
C(25)-C(22)-C(23)	105.1(2)	C(22)-C(25')-H(25E)	109.5
C(10)-C(22)-C(23)	111.93(17)	H(25D)-C(25')-H(25E)	109.5
C(24')-C(22)-C(23')	108.0(3)	C(22)-C(25')-H(25F)	109.5
C(25')-C(22)-C(23')	105.2(3)	H(25D)-C(25')-H(25F)	109.5
C(10)-C(22)-C(23')	110.3(2)	H(25E)-C(25')-H(25F)	109.5
C(22)-C(23)-H(23A)	109.5	C(29)-C(26)-C(12)	112.43(14)
C(22)-C(23)-H(23B)	109.5	C(29)-C(26)-C(27)	107.70(15)
H(23A)-C(23)-H(23B)	109.5	C(12)-C(26)-C(27)	109.91(13)
C(22)-C(23)-H(23C)	109.5	C(29)-C(26)-C(28)	108.60(14)
H(23A)-C(23)-H(23C)	109.5	C(12)-C(26)-C(28)	108.49(14)
H(23B)-C(23)-H(23C)	109.5	C(27)-C(26)-C(28)	109.69(15)
C(22)-C(24)-H(24A)	109.5	C(26)-C(27)-H(27A)	109.5
C(22)-C(24)-H(24B)	109.5	C(26)-C(27)-H(27B)	109.5
H(24A)-C(24)-H(24B)	109.5	H(27A)-C(27)-H(27B)	109.5
C(22)-C(24)-H(24C)	109.5	C(26)-C(27)-H(27C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(27A)-C(27)-H(27C)	109.5
H(24B)-C(24)-H(24C)	109.5	H(27B)-C(27)-H(27C)	109.5
C(22)-C(25)-H(25A)	109.5	C(26)-C(28)-H(28A)	109.5
C(22)-C(25)-H(25B)	109.5	C(26)-C(28)-H(28B)	109.5
H(25A)-C(25)-H(25B)	109.5	H(28A)-C(28)-H(28B)	109.5
C(22)-C(25)-H(25C)	109.5	C(26)-C(28)-H(28C)	109.5
H(25A)-C(25)-H(25C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(25B)-C(25)-H(25C)	109.5	H(28B)-C(28)-H(28C)	109.5
C(22)-C(23')-H(23D)	109.5	C(26)-C(29)-H(29A)	109.5

C(26)-C(29)-H(29B)	109.5	H(29A)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5	H(29B)-C(29)-H(29C)	109.5
C(26)-C(29)-H(29C)	109.5		

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Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1

Table S4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk01. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12} ]$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
P1	20(1)	19(1)	21(1)	-2(1)	5(1)	-1(1)
C1	18(1)	17(1)	23(1)	-2(1)	3(1)	-1(1)
C2	22(1)	19(1)	16(1)	1(1)	2(1)	0(1)
C3	21(1)	22(1)	17(1)	0(1)	4(1)	-1(1)
C4	26(1)	20(1)	15(1)	2(1)	2(1)	-2(1)
C5	30(1)	17(1)	19(1)	2(1)	4(1)	3(1)
C6	23(1)	22(1)	17(1)	4(1)	4(1)	3(1)
C7	21(1)	20(1)	19(1)	2(1)	4(1)	-1(1)
C8	22(1)	19(1)	20(1)	-3(1)	2(1)	1(1)
C9	32(1)	20(1)	22(1)	0(1)	1(1)	3(1)
C10	35(1)	25(1)	22(1)	-3(1)	-6(1)	6(1)
C11	25(1)	28(1)	29(1)	-6(1)	-8(1)	0(1)
C12	21(1)	25(1)	27(1)	-4(1)	0(1)	-2(1)
C13	21(1)	23(1)	20(1)	-5(1)	0(1)	-1(1)
C14	33(1)	21(1)	24(1)	-2(1)	6(1)	-7(1)
C15	58(2)	39(2)	31(2)	-10(1)	12(2)	-22(2)
C16	67(2)	41(2)	39(2)	18(2)	-7(2)	-28(2)
C17	39(2)	33(2)	93(3)	-17(2)	30(2)	-18(1)
C15'	83(8)	36(5)	57(6)	-21(4)	37(5)	-28(5)
C16'	57(5)	31(4)	28(3)	6(3)	5(3)	-19(4)
C17'	38(4)	38(4)	88(7)	23(5)	-24(5)	-20(3)
C18	26(1)	26(1)	27(1)	6(1)	9(1)	5(1)
C19	23(1)	43(1)	35(1)	6(1)	5(1)	7(1)
C20	38(1)	34(1)	43(1)	3(1)	18(1)	12(1)
C21	33(1)	40(1)	29(1)	9(1)	13(1)	7(1)
C22	52(1)	29(1)	22(1)	2(1)	-12(1)	-1(1)
C23	78(3)	47(2)	17(1)	8(1)	-7(2)	-10(2)
C24	62(3)	60(3)	40(2)	7(2)	-24(2)	11(2)
C25	94(3)	35(2)	22(1)	-3(1)	-6(2)	-12(2)
C23'	61(3)	49(3)	23(2)	6(2)	-17(2)	-20(3)
C24'	60(3)	80(5)	20(2)	-9(2)	-3(2)	10(3)

C25'	59(3)	37(3)	32(2)	14(2)	-14(2)	-9(2)
C26	23(1)	34(1)	32(1)	-4(1)	1(1)	-10(1)
C27	38(1)	44(1)	49(1)	13(1)	-1(1)	-15(1)
C28	36(1)	51(1)	40(1)	-13(1)	14(1)	-14(1)
C29	29(1)	45(1)	45(1)	-11(1)	3(1)	-15(1)

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Table S5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk01.

	x	y	z	U(eq)
H1A	9041	39	5181	23
H1B	9504	-644	4574	23
H3	10104	1669	3071	24
H5	8280	3004	4442	26
H7	7647	913	3878	24
H9	8346	120	387	30
H11	6150	-1142	734	34
H13	7850	-549	4010	26
H15A	9431	3691	5056	63
H15B	10433	3944	4772	63
H15C	10325	3240	5643	63
H16A	8880	3696	2627	75
H16B	9450	3270	1635	75
H16C	9881	3973	2385	75
H17A	11288	3289	3332	80
H17B	10851	2621	2478	80
H17C	11183	2531	4037	80
H15D	10153	4115	4378	84
H15E	9631	3615	5323	84
H15F	9083	3929	3975	84
H16D	10161	2813	1779	58
H16E	10452	3619	2183	58
H16F	9385	3415	1826	58
H17D	11131	2422	3889	87
H17E	10896	2743	5268	87
H17F	11361	3243	4259	87
H19A	6120	2066	2863	50
H19B	5508	1883	4016	50
H19C	6195	1293	3555	50
H20A	6682	3150	4203	56

H20B	7160	3055	5706	56
H20C	6078	2910	5333	56
H21A	6280	1704	6354	50
H21B	7366	1838	6711	50
H21C	6998	1148	5864	50
H23A	7683	444	-1646	73
H23B	7480	-83	-2897	73
H23C	8274	-275	-1706	73
H24A	5543	-354	-1134	86
H24B	5857	-121	-2525	86
H24C	6078	387	-1250	86
H25A	6466	-1531	-1351	77
H25B	7538	-1455	-1503	77
H25C	6769	-1230	-2705	77
H23D	5833	-951	-2573	70
H23E	5500	-786	-1163	70
H23F	6135	-1470	-1335	70
H24D	7485	-753	-2826	81
H24E	7772	-1281	-1597	81
H24F	8228	-501	-1612	81
H25D	6408	289	-2503	66
H25E	7169	586	-1351	66
H25F	6148	412	-1036	66
H27A	6617	-2090	4927	66
H27B	7445	-1532	4892	66
H27C	7293	-2163	3816	66
H28A	5522	-1057	4860	62
H28B	5445	-497	3654	62
H28C	6335	-493	4759	62
H29A	5287	-2085	3267	60
H29B	5899	-2140	2074	60
H29C	5161	-1506	2090	60

Table S6. Torsion angles [°] for neijk01.

C8-P1-C1-C1#1	173.33(13)	C3-C4-C14-C16'	68.6(5)
C2-P1-C1-C1#1	-81.81(14)	C5-C4-C14-C16'	-108.5(5)
C8-P1-C2-C7	31.62(13)	C3-C4-C14-C15	-134.5(2)
C1-P1-C2-C7	-71.97(13)	C5-C4-C14-C15	48.4(3)
C8-P1-C2-C3	-150.49(11)	C3-C4-C14-C17	-11.1(3)
C1-P1-C2-C3	105.91(11)	C5-C4-C14-C17	171.7(3)
C7-C2-C3-C4	0.6(2)	C3-C4-C14-C15'	-166.7(6)
P1-C2-C3-C4	-177.39(11)	C5-C4-C14-C15'	16.2(6)
C2-C3-C4-C5	-0.2(2)	C3-C4-C14-C16	107.7(3)
C2-C3-C4-C14	-177.36(13)	C5-C4-C14-C16	-69.4(3)
C3-C4-C5-C6	-0.1(2)	C3-C4-C14-C17'	-50.7(6)
C14-C4-C5-C6	177.09(13)	C5-C4-C14-C17'	132.2(6)
C4-C5-C6-C7	0.0(2)	C5-C6-C18-C20	6.1(2)
C4-C5-C6-C18	178.56(13)	C7-C6-C18-C20	-175.37(14)
C3-C2-C7-C6	-0.7(2)	C5-C6-C18-C19	126.32(15)
P1-C2-C7-C6	177.12(11)	C7-C6-C18-C19	-55.13(18)
C5-C6-C7-C2	0.4(2)	C5-C6-C18-C21	-114.30(16)
C18-C6-C7-C2	-178.18(13)	C7-C6-C18-C21	64.25(18)
C2-P1-C8-C13	-88.98(13)	C9-C10-C22-C24'	59.3(3)
C1-P1-C8-C13	13.12(14)	C11-C10-C22-C24'	-119.9(3)
C2-P1-C8-C9	95.61(12)	C9-C10-C22-C25'	-67.6(3)
C1-P1-C8-C9	-162.29(12)	C11-C10-C22-C25'	113.2(3)
C13-C8-C9-C10	0.3(2)	C9-C10-C22-C24	-114.9(2)
P1-C8-C9-C10	175.92(12)	C11-C10-C22-C24	65.9(3)
C8-C9-C10-C11	-0.8(2)	C9-C10-C22-C25	119.6(2)
C8-C9-C10-C22	179.99(15)	C11-C10-C22-C25	-59.6(3)
C9-C10-C11-C12	0.5(2)	C9-C10-C22-C23	3.4(3)
C22-C10-C11-C12	179.77(15)	C11-C10-C22-C23	-175.8(2)
C10-C11-C12-C13	0.2(2)	C9-C10-C22-C23'	178.5(3)
C10-C11-C12-C26	179.72(15)	C11-C10-C22-C23'	-0.7(3)
C9-C8-C13-C12	0.6(2)	C11-C12-C26-C29	9.2(2)
P1-C8-C13-C12	-174.81(12)	C13-C12-C26-C29	-171.28(15)
C11-C12-C13-C8	-0.8(2)	C11-C12-C26-C27	129.19(17)
C26-C12-C13-C8	179.70(14)	C13-C12-C26-C27	-51.3(2)

C11-C12-C26-C28	-110.88(17)	C13-C12-C26-C28	68.60(19)
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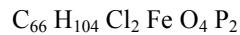
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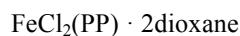
### 3.2 FeCl<sub>2</sub>(<sup>t</sup>Bu<sup>u</sup>dppe)

REFERENCE NUMBER: neijk04

#### CRYSTAL STRUCTURE REPORT



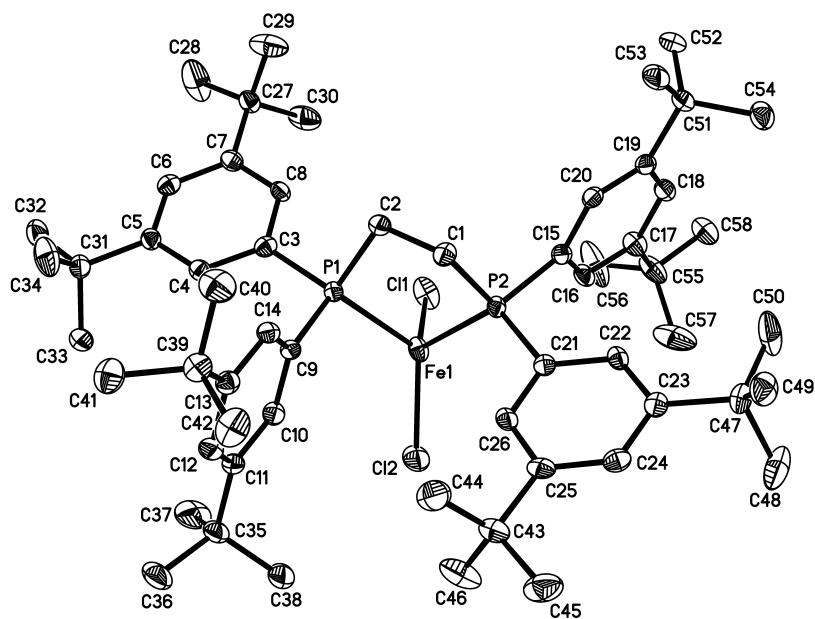
or



Report prepared for:

J. Kneebone, Prof. M. Neidig

February 11, 2013



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#### Data collection

A crystal ( $0.48 \times 0.16 \times 0.12 \text{ mm}^3$ ) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at  $100.0(5) \text{ K}$ .<sup>1</sup> A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: three major sections of frames were collected with  $0.50^\circ$  steps in  $\omega$  at three different  $\phi$  settings and a detector position of  $-38^\circ$  in  $2\theta$ . The intensity data were corrected for absorption.<sup>2</sup> Final cell constants were calculated from the xyz centroids of 4038 strong reflections from the actual data collection after integration.<sup>3</sup> See Table 1 for additional crystal and refinement information.

#### Structure solution and refinement

The structure was solved using SIR97<sup>4</sup> and refined using SHELXL-2012.<sup>5</sup> The space group  $P2_1/c$  was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to  $R1 = 0.0618 (F^2, I > 2\sigma(I))$  and  $wR2 = 0.1649 (F^2, \text{all data})$ .

#### Structure description

The structure is the one suggested, with all atoms in general positions. There are two cocrystallized dioxane solvent molecules per iron molecule. One *tert*-butyl group is modeled as disordered over two positions (89:11).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

<sup>1</sup> APEX2, version 2012.4-3; Bruker AXS: Madison, WI, 2012.

<sup>2</sup> Sheldrick, G. M. SADABS, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

<sup>3</sup> SAINT, version 7.68A; Bruker AXS: Madison, WI, 2009.

<sup>4</sup> Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: A new program for solving and refining crystal structures; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

<sup>5</sup> Sheldrick, G. M. SHELXL-2012 University of Göttingen: Göttingen, Germany, 2012.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_{\text{o}}^2 - \langle F_{\text{o}}^2 \rangle| / \Sigma |F_{\text{o}}^2|$$

$$R1 = \Sigma ||F_{\text{o}}|| - |F_{\text{c}}|| / \Sigma |F_{\text{o}}|$$

$$wR2 = [\Sigma [w(F_{\text{o}}^2 - F_{\text{c}}^2)^2] / \Sigma [w(F_{\text{o}}^2)^2]]^{1/2}$$

where  $w = 1 / [\sigma^2(F_{\text{o}}^2) + (aP)^2 + bP]$  and

$$P = 1/3 \max(0, F_{\text{o}}^2) + 2/3 F_{\text{c}}^2$$

$$\text{GOF} = S = [\Sigma [w(F_{\text{o}}^2 - F_{\text{c}}^2)^2] / (m-n)]^{1/2}$$

where  $m$  = number of reflections and  $n$  = number of parameters

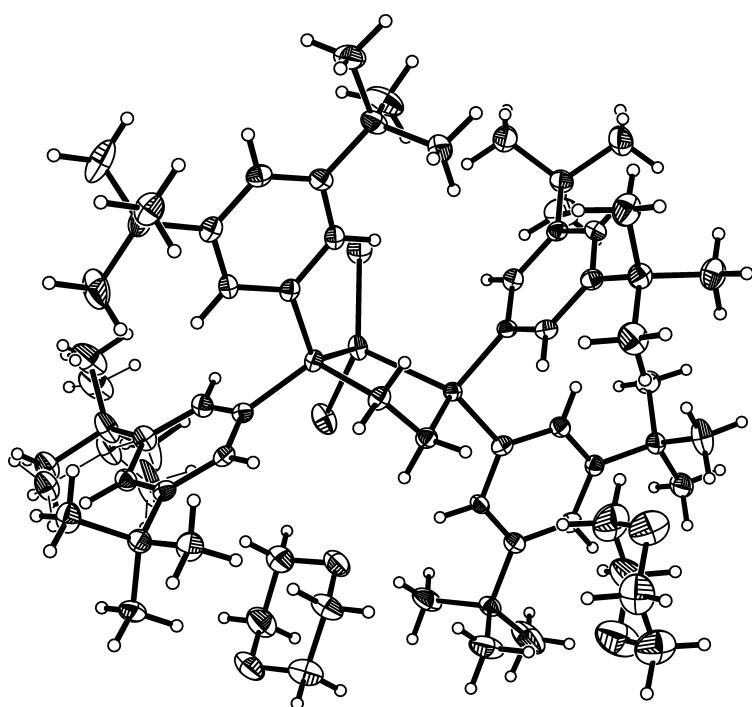


Table S7. Crystal data and structure refinement for neijk04.

Identification code	neijk04		
Empirical formula	C66 H104 Cl2 Fe O4 P2		
Formula weight	1150.18		
Temperature	100.0(5) K		
Wavelength	0.71073 Å		
Crystal system	monoclinic		
Space group	<i>P</i> 2 <sub>1</sub> /c		
Unit cell dimensions	<i>a</i> = 14.135(4) Å	$\alpha$ = 90°	
	<i>b</i> = 28.716(8) Å	$\beta$ = 102.479(6)°	
	<i>c</i> = 16.870(5) Å	$\gamma$ = 90°	
Volume	6686(3) Å <sup>3</sup>		
<i>Z</i>	4		
Density (calculated)	1.143 Mg/m <sup>3</sup>		
Absorption coefficient	0.396 mm <sup>-1</sup>		
<i>F</i> (000)	2488		
Crystal color, morphology	colorless, needle		
Crystal size	0.48 x 0.16 x 0.12 mm <sup>3</sup>		
Theta range for data collection	1.425 to 29.574°		
Index ranges	-19 ≤ <i>h</i> ≤ 19, -38 ≤ <i>k</i> ≤ 39, -23 ≤ <i>l</i> ≤ 23		
Reflections collected	78114		
Independent reflections	18751 [ <i>R</i> (int) = 0.0998]		
Observed reflections	10927		
Completeness to theta = 29.575°	99.9%		
Absorption correction	Multi-scan		
Max. and min. transmission	0.7461 and 0.6845		
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>		
Data / restraints / parameters	18751 / 7 / 713		
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.017		
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> 1 = 0.0618, <i>wR</i> 2 = 0.1419		
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1193, <i>wR</i> 2 = 0.1649		
Largest diff. peak and hole	1.687 and -0.786 e.Å <sup>-3</sup>		

Table S8. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk04.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
Fe1	7787(1)	2417(1)	5510(1)	20(1)
Cl1	9363(1)	2543(1)	5688(1)	33(1)
Cl2	6910(1)	2231(1)	4293(1)	33(1)
P1	7192(1)	3029(1)	6269(1)	17(1)
P2	7415(1)	1921(1)	6587(1)	16(1)
C1	6956(2)	2306(1)	7294(2)	20(1)
C2	7347(2)	2801(1)	7294(2)	19(1)
C3	7724(2)	3607(1)	6414(2)	19(1)
C4	7223(2)	3993(1)	6031(2)	19(1)
C5	7646(2)	4433(1)	6099(2)	19(1)
C6	8591(2)	4477(1)	6565(2)	20(1)
C7	9098(2)	4098(1)	6966(2)	20(1)
C8	8657(2)	3660(1)	6881(2)	18(1)
C9	5911(2)	3136(1)	5867(2)	17(1)
C10	5634(2)	3160(1)	5026(2)	20(1)
C11	4692(2)	3282(1)	4636(2)	20(1)
C12	4040(2)	3362(1)	5125(2)	21(1)
C13	4288(2)	3336(1)	5975(2)	19(1)
C14	5236(2)	3225(1)	6340(2)	17(1)
C15	8459(2)	1605(1)	7141(2)	17(1)
C16	9095(2)	1436(1)	6689(2)	20(1)
C17	9877(2)	1155(1)	7034(2)	23(1)
C18	9998(2)	1048(1)	7854(2)	21(1)
C19	9375(2)	1214(1)	8332(2)	19(1)
C20	8609(2)	1493(1)	7966(2)	18(1)
C21	6468(2)	1484(1)	6379(2)	17(1)
C22	6596(2)	1033(1)	6691(2)	17(1)
C23	5838(2)	715(1)	6546(2)	19(1)
C24	4942(2)	860(1)	6082(2)	21(1)
C25	4796(2)	1304(1)	5763(2)	20(1)
C26	5573(2)	1615(1)	5912(2)	19(1)

C27	10110(2)	4146(1)	7516(2)	22(1)
C28	10538(3)	4627(1)	7474(3)	67(1)
C29	10055(2)	4044(1)	8390(2)	43(1)
C30	10794(2)	3795(1)	7259(2)	37(1)
C31	7062(2)	4846(1)	5671(2)	23(1)
C32	7659(2)	5286(1)	5715(2)	34(1)
C33	6671(2)	4735(1)	4771(2)	32(1)
C34	6210(2)	4938(1)	6073(2)	41(1)
C35	4422(2)	3310(1)	3708(2)	26(1)
C36	3442(3)	3550(1)	3401(2)	43(1)
C37	5194(3)	3584(1)	3392(2)	45(1)
C38	4366(3)	2818(1)	3360(2)	36(1)
C39	3514(2)	3437(1)	6457(2)	23(1)
C40	3920(2)	3423(1)	7370(2)	35(1)
C41	3096(2)	3924(1)	6235(2)	32(1)
C42	2694(2)	3075(1)	6242(2)	35(1)
C43	3821(2)	1472(1)	5253(2)	25(1)
C44	3447(2)	1865(1)	5698(2)	43(1)
C45	3061(2)	1080(1)	5106(2)	39(1)
C46	3965(3)	1625(1)	4427(2)	47(1)
C47	5956(2)	216(1)	6881(2)	24(1)
C48	5793(3)	-127(1)	6171(2)	45(1)
C49	5213(2)	122(1)	7400(2)	31(1)
C50	6963(2)	135(1)	7414(2)	46(1)
C51	9554(2)	1078(1)	9232(2)	23(1)
C52	10550(2)	1260(1)	9670(2)	31(1)
C53	8787(2)	1280(1)	9646(2)	29(1)
C54	9526(2)	545(1)	9304(2)	28(1)
C55	10550(4)	989(2)	6490(3)	31(1)
C56	10989(5)	1426(2)	6172(5)	55(2)
C57	9988(6)	700(3)	5784(3)	56(2)
C58	11385(4)	693(2)	6958(4)	32(1)
C55'	10785(19)	1062(13)	6700(20)	31(1)
C56'	11340(40)	1515(13)	6570(40)	55(2)
C57'	10370(40)	841(19)	5880(20)	56(2)
C58'	11540(30)	735(15)	7190(30)	32(1)

O1	6022(2)	4123(1)	8666(2)	51(1)
C59	6532(3)	4111(1)	9495(2)	49(1)
C60	7258(3)	4488(2)	9657(2)	54(1)
O2	7931(2)	4449(1)	9153(2)	67(1)
C61	7428(3)	4455(2)	8337(2)	52(1)
C62	6698(3)	4079(2)	8158(2)	56(1)
O3	9884(2)	2731(1)	8017(1)	34(1)
C63	9928(2)	2641(1)	8855(2)	34(1)
C64	10938(2)	2722(1)	9351(2)	40(1)
O4	11630(2)	2441(1)	9066(2)	42(1)
C65	11573(2)	2533(1)	8236(2)	45(1)
C66	10573(2)	2441(1)	7748(2)	42(1)

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Table S9. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for neijk04.

Fe(1)-Cl(1)	2.2120(10)	C(13)-C(14)	1.386(4)
Fe(1)-Cl(2)	2.2225(10)	C(13)-C(39)	1.526(4)
Fe(1)-P(1)	2.4291(9)	C(14)-H(14)	0.9500
Fe(1)-P(2)	2.4549(9)	C(15)-C(16)	1.386(4)
P(1)-C(9)	1.816(3)	C(15)-C(20)	1.400(4)
P(1)-C(3)	1.818(3)	C(16)-C(17)	1.390(4)
P(1)-C(2)	1.818(3)	C(16)-H(16)	0.9500
P(2)-C(15)	1.810(3)	C(17)-C(18)	1.390(4)
P(2)-C(21)	1.811(3)	C(17)-C(55)	1.533(4)
P(2)-C(1)	1.845(3)	C(17)-C(55')	1.537(10)
C(1)-C(2)	1.526(4)	C(18)-C(19)	1.399(4)
C(1)-H(1A)	0.9900	C(18)-H(18)	0.9500
C(1)-H(1B)	0.9900	C(19)-C(20)	1.382(4)
C(2)-H(2A)	0.9900	C(19)-C(51)	1.534(4)
C(2)-H(2B)	0.9900	C(20)-H(20)	0.9500
C(3)-C(8)	1.390(3)	C(21)-C(26)	1.390(4)
C(3)-C(4)	1.396(4)	C(21)-C(22)	1.396(4)
C(4)-C(5)	1.392(4)	C(22)-C(23)	1.388(4)
C(4)-H(4)	0.9500	C(22)-H(22)	0.9500
C(5)-C(6)	1.402(4)	C(23)-C(24)	1.400(4)
C(5)-C(31)	1.533(4)	C(23)-C(47)	1.537(4)
C(6)-C(7)	1.395(4)	C(24)-C(25)	1.383(4)
C(6)-H(6)	0.9500	C(24)-H(24)	0.9500
C(7)-C(8)	1.396(4)	C(25)-C(26)	1.395(4)
C(7)-C(27)	1.534(4)	C(25)-C(43)	1.536(4)
C(8)-H(8)	0.9500	C(26)-H(26)	0.9500
C(9)-C(10)	1.390(4)	C(27)-C(28)	1.515(4)
C(9)-C(14)	1.394(4)	C(27)-C(29)	1.521(4)
C(10)-C(11)	1.397(4)	C(27)-C(30)	1.525(4)
C(10)-H(10)	0.9500	C(28)-H(28A)	0.9800
C(11)-C(12)	1.382(4)	C(28)-H(28B)	0.9800
C(11)-C(35)	1.531(4)	C(28)-H(28C)	0.9800
C(12)-C(13)	1.402(4)	C(29)-H(29A)	0.9800
C(12)-H(12)	0.9500	C(29)-H(29B)	0.9800

C(29)-H(29C)	0.9800	C(41)-H(41C)	0.9800
C(30)-H(30A)	0.9800	C(42)-H(42A)	0.9800
C(30)-H(30B)	0.9800	C(42)-H(42B)	0.9800
C(30)-H(30C)	0.9800	C(42)-H(42C)	0.9800
C(31)-C(32)	1.513(4)	C(43)-C(44)	1.513(4)
C(31)-C(34)	1.527(4)	C(43)-C(46)	1.517(4)
C(31)-C(33)	1.534(4)	C(43)-C(45)	1.540(4)
C(32)-H(32A)	0.9800	C(44)-H(44A)	0.9800
C(32)-H(32B)	0.9800	C(44)-H(44B)	0.9800
C(32)-H(32C)	0.9800	C(44)-H(44C)	0.9800
C(33)-H(33A)	0.9800	C(45)-H(45A)	0.9800
C(33)-H(33B)	0.9800	C(45)-H(45B)	0.9800
C(33)-H(33C)	0.9800	C(45)-H(45C)	0.9800
C(34)-H(34A)	0.9800	C(46)-H(46A)	0.9800
C(34)-H(34B)	0.9800	C(46)-H(46B)	0.9800
C(34)-H(34C)	0.9800	C(46)-H(46C)	0.9800
C(35)-C(38)	1.525(4)	C(47)-C(50)	1.528(4)
C(35)-C(37)	1.533(4)	C(47)-C(48)	1.530(4)
C(35)-C(36)	1.534(4)	C(47)-C(49)	1.531(4)
C(36)-H(36A)	0.9800	C(48)-H(48A)	0.9800
C(36)-H(36B)	0.9800	C(48)-H(48B)	0.9800
C(36)-H(36C)	0.9800	C(48)-H(48C)	0.9800
C(37)-H(37A)	0.9800	C(49)-H(49A)	0.9800
C(37)-H(37B)	0.9800	C(49)-H(49B)	0.9800
C(37)-H(37C)	0.9800	C(49)-H(49C)	0.9800
C(38)-H(38A)	0.9800	C(50)-H(50A)	0.9800
C(38)-H(38B)	0.9800	C(50)-H(50B)	0.9800
C(38)-H(38C)	0.9800	C(50)-H(50C)	0.9800
C(39)-C(40)	1.523(4)	C(51)-C(53)	1.525(4)
C(39)-C(41)	1.534(4)	C(51)-C(52)	1.533(4)
C(39)-C(42)	1.541(4)	C(51)-C(54)	1.537(4)
C(40)-H(40A)	0.9800	C(52)-H(52A)	0.9800
C(40)-H(40B)	0.9800	C(52)-H(52B)	0.9800
C(40)-H(40C)	0.9800	C(52)-H(52C)	0.9800
C(41)-H(41A)	0.9800	C(53)-H(53A)	0.9800
C(41)-H(41B)	0.9800	C(53)-H(53B)	0.9800

C(53)-H(53C)	0.9800	O(2)-C(61)	1.407(4)
C(54)-H(54A)	0.9800	C(61)-C(62)	1.479(6)
C(54)-H(54B)	0.9800	C(61)-H(61A)	0.9900
C(54)-H(54C)	0.9800	C(61)-H(61B)	0.9900
C(55)-C(57)	1.527(6)	C(62)-H(62A)	0.9900
C(55)-C(58)	1.529(5)	C(62)-H(62B)	0.9900
C(55)-C(56)	1.546(5)	O(3)-C(63)	1.425(4)
C(56)-H(56A)	0.9800	O(3)-C(66)	1.428(4)
C(56)-H(56B)	0.9800	C(63)-C(64)	1.508(4)
C(56)-H(56C)	0.9800	C(63)-H(63A)	0.9900
C(57)-H(57A)	0.9800	C(63)-H(63B)	0.9900
C(57)-H(57B)	0.9800	C(64)-O(4)	1.430(4)
C(57)-H(57C)	0.9800	C(64)-H(64A)	0.9900
C(58)-H(58A)	0.9800	C(64)-H(64B)	0.9900
C(58)-H(58B)	0.9800	O(4)-C(65)	1.410(4)
C(58)-H(58C)	0.9800	C(65)-C(66)	1.498(5)
C(55')-C(57')	1.509(19)	C(65)-H(65A)	0.9900
C(55')-C(58')	1.532(18)	C(65)-H(65B)	0.9900
C(55')-C(56')	1.555(19)	C(66)-H(66A)	0.9900
C(56')-H(56D)	0.9800	C(66)-H(66B)	0.9900
C(56')-H(56E)	0.9800	Cl(1)-Fe(1)-Cl(2)	120.65(4)
C(56')-H(56F)	0.9800	Cl(1)-Fe(1)-P(1)	105.28(3)
C(57')-H(57D)	0.9800	Cl(2)-Fe(1)-P(1)	118.25(3)
C(57')-H(57E)	0.9800	Cl(1)-Fe(1)-P(2)	111.39(3)
C(57')-H(57F)	0.9800	Cl(2)-Fe(1)-P(2)	112.20(4)
C(58')-H(58D)	0.9800	P(1)-Fe(1)-P(2)	82.85(3)
C(58')-H(58E)	0.9800	C(9)-P(1)-C(3)	104.28(12)
C(58')-H(58F)	0.9800	C(9)-P(1)-C(2)	108.75(12)
O(1)-C(62)	1.419(4)	C(3)-P(1)-C(2)	103.83(12)
O(1)-C(59)	1.429(4)	C(9)-P(1)-Fe(1)	110.86(9)
C(59)-C(60)	1.475(5)	C(3)-P(1)-Fe(1)	123.44(9)
C(59)-H(59A)	0.9900	C(2)-P(1)-Fe(1)	104.90(9)
C(59)-H(59B)	0.9900	C(15)-P(2)-C(21)	103.85(12)
C(60)-O(2)	1.410(4)	C(15)-P(2)-C(1)	109.18(13)
C(60)-H(60A)	0.9900	C(21)-P(2)-C(1)	101.05(12)
C(60)-H(60B)	0.9900	C(15)-P(2)-Fe(1)	113.05(9)

C(21)-P(2)-Fe(1)	121.71(9)	C(9)-C(10)-H(10)	119.3
C(1)-P(2)-Fe(1)	107.00(9)	C(11)-C(10)-H(10)	119.3
C(2)-C(1)-P(2)	112.36(18)	C(12)-C(11)-C(10)	116.9(2)
C(2)-C(1)-H(1A)	109.1	C(12)-C(11)-C(35)	123.4(2)
P(2)-C(1)-H(1A)	109.1	C(10)-C(11)-C(35)	119.7(2)
C(2)-C(1)-H(1B)	109.1	C(11)-C(12)-C(13)	123.3(2)
P(2)-C(1)-H(1B)	109.1	C(11)-C(12)-H(12)	118.4
H(1A)-C(1)-H(1B)	107.9	C(13)-C(12)-H(12)	118.4
C(1)-C(2)-P(1)	111.48(18)	C(14)-C(13)-C(12)	118.1(2)
C(1)-C(2)-H(2A)	109.3	C(14)-C(13)-C(39)	122.8(2)
P(1)-C(2)-H(2A)	109.3	C(12)-C(13)-C(39)	119.0(2)
C(1)-C(2)-H(2B)	109.3	C(13)-C(14)-C(9)	120.2(2)
P(1)-C(2)-H(2B)	109.3	C(13)-C(14)-H(14)	119.9
H(2A)-C(2)-H(2B)	108.0	C(9)-C(14)-H(14)	119.9
C(8)-C(3)-C(4)	120.0(2)	C(16)-C(15)-C(20)	119.3(2)
C(8)-C(3)-P(1)	119.4(2)	C(16)-C(15)-P(2)	116.5(2)
C(4)-C(3)-P(1)	120.6(2)	C(20)-C(15)-P(2)	124.0(2)
C(5)-C(4)-C(3)	121.1(2)	C(15)-C(16)-C(17)	121.6(3)
C(5)-C(4)-H(4)	119.5	C(15)-C(16)-H(16)	119.2
C(3)-C(4)-H(4)	119.5	C(17)-C(16)-H(16)	119.2
C(4)-C(5)-C(6)	117.9(2)	C(16)-C(17)-C(18)	117.4(2)
C(4)-C(5)-C(31)	119.0(2)	C(16)-C(17)-C(55)	118.0(3)
C(6)-C(5)-C(31)	123.1(2)	C(18)-C(17)-C(55)	124.6(3)
C(7)-C(6)-C(5)	122.0(2)	C(16)-C(17)-C(55')	126.7(13)
C(7)-C(6)-H(6)	119.0	C(18)-C(17)-C(55')	113.5(15)
C(5)-C(6)-H(6)	119.0	C(17)-C(18)-C(19)	122.8(2)
C(6)-C(7)-C(8)	118.8(2)	C(17)-C(18)-H(18)	118.6
C(6)-C(7)-C(27)	122.4(2)	C(19)-C(18)-H(18)	118.6
C(8)-C(7)-C(27)	118.8(2)	C(20)-C(19)-C(18)	118.0(2)
C(3)-C(8)-C(7)	120.3(2)	C(20)-C(19)-C(51)	122.3(2)
C(3)-C(8)-H(8)	119.9	C(18)-C(19)-C(51)	119.7(2)
C(7)-C(8)-H(8)	119.9	C(19)-C(20)-C(15)	120.9(2)
C(10)-C(9)-C(14)	119.9(2)	C(19)-C(20)-H(20)	119.5
C(10)-C(9)-P(1)	115.3(2)	C(15)-C(20)-H(20)	119.5
C(14)-C(9)-P(1)	124.6(2)	C(26)-C(21)-C(22)	119.4(2)
C(9)-C(10)-C(11)	121.5(3)	C(26)-C(21)-P(2)	117.9(2)

C(22)-C(21)-P(2)	122.7(2)	H(30A)-C(30)-H(30B)	109.5
C(23)-C(22)-C(21)	120.8(2)	C(27)-C(30)-H(30C)	109.5
C(23)-C(22)-H(22)	119.6	H(30A)-C(30)-H(30C)	109.5
C(21)-C(22)-H(22)	119.6	H(30B)-C(30)-H(30C)	109.5
C(22)-C(23)-C(24)	118.3(2)	C(32)-C(31)-C(34)	108.5(3)
C(22)-C(23)-C(47)	122.0(2)	C(32)-C(31)-C(5)	112.6(2)
C(24)-C(23)-C(47)	119.7(2)	C(34)-C(31)-C(5)	108.8(2)
C(25)-C(24)-C(23)	122.1(3)	C(32)-C(31)-C(33)	107.4(2)
C(25)-C(24)-H(24)	118.9	C(34)-C(31)-C(33)	109.0(3)
C(23)-C(24)-H(24)	118.9	C(5)-C(31)-C(33)	110.3(2)
C(24)-C(25)-C(26)	118.3(2)	C(31)-C(32)-H(32A)	109.5
C(24)-C(25)-C(43)	123.3(2)	C(31)-C(32)-H(32B)	109.5
C(26)-C(25)-C(43)	118.4(2)	H(32A)-C(32)-H(32B)	109.5
C(21)-C(26)-C(25)	121.0(2)	C(31)-C(32)-H(32C)	109.5
C(21)-C(26)-H(26)	119.5	H(32A)-C(32)-H(32C)	109.5
C(25)-C(26)-H(26)	119.5	H(32B)-C(32)-H(32C)	109.5
C(28)-C(27)-C(29)	109.0(3)	C(31)-C(33)-H(33A)	109.5
C(28)-C(27)-C(30)	107.8(3)	C(31)-C(33)-H(33B)	109.5
C(29)-C(27)-C(30)	108.5(3)	H(33A)-C(33)-H(33B)	109.5
C(28)-C(27)-C(7)	112.6(2)	C(31)-C(33)-H(33C)	109.5
C(29)-C(27)-C(7)	109.5(2)	H(33A)-C(33)-H(33C)	109.5
C(30)-C(27)-C(7)	109.4(2)	H(33B)-C(33)-H(33C)	109.5
C(27)-C(28)-H(28A)	109.5	C(31)-C(34)-H(34A)	109.5
C(27)-C(28)-H(28B)	109.5	C(31)-C(34)-H(34B)	109.5
H(28A)-C(28)-H(28B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(27)-C(28)-H(28C)	109.5	C(31)-C(34)-H(34C)	109.5
H(28A)-C(28)-H(28C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(28B)-C(28)-H(28C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(27)-C(29)-H(29A)	109.5	C(38)-C(35)-C(11)	109.1(2)
C(27)-C(29)-H(29B)	109.5	C(38)-C(35)-C(37)	109.0(3)
H(29A)-C(29)-H(29B)	109.5	C(11)-C(35)-C(37)	110.1(2)
C(27)-C(29)-H(29C)	109.5	C(38)-C(35)-C(36)	108.6(3)
H(29A)-C(29)-H(29C)	109.5	C(11)-C(35)-C(36)	112.1(2)
H(29B)-C(29)-H(29C)	109.5	C(37)-C(35)-C(36)	108.0(3)
C(27)-C(30)-H(30A)	109.5	C(35)-C(36)-H(36A)	109.5
C(27)-C(30)-H(30B)	109.5	C(35)-C(36)-H(36B)	109.5

H(36A)-C(36)-H(36B)	109.5	H(42A)-C(42)-H(42B)	109.5
C(35)-C(36)-H(36C)	109.5	C(39)-C(42)-H(42C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(42A)-C(42)-H(42C)	109.5
H(36B)-C(36)-H(36C)	109.5	H(42B)-C(42)-H(42C)	109.5
C(35)-C(37)-H(37A)	109.5	C(44)-C(43)-C(46)	111.7(3)
C(35)-C(37)-H(37B)	109.5	C(44)-C(43)-C(25)	108.9(2)
H(37A)-C(37)-H(37B)	109.5	C(46)-C(43)-C(25)	108.8(2)
C(35)-C(37)-H(37C)	109.5	C(44)-C(43)-C(45)	108.7(3)
H(37A)-C(37)-H(37C)	109.5	C(46)-C(43)-C(45)	107.0(3)
H(37B)-C(37)-H(37C)	109.5	C(25)-C(43)-C(45)	111.7(2)
C(35)-C(38)-H(38A)	109.5	C(43)-C(44)-H(44A)	109.5
C(35)-C(38)-H(38B)	109.5	C(43)-C(44)-H(44B)	109.5
H(38A)-C(38)-H(38B)	109.5	H(44A)-C(44)-H(44B)	109.5
C(35)-C(38)-H(38C)	109.5	C(43)-C(44)-H(44C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(44A)-C(44)-H(44C)	109.5
H(38B)-C(38)-H(38C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(40)-C(39)-C(13)	112.2(2)	C(43)-C(45)-H(45A)	109.5
C(40)-C(39)-C(41)	108.1(2)	C(43)-C(45)-H(45B)	109.5
C(13)-C(39)-C(41)	109.1(2)	H(45A)-C(45)-H(45B)	109.5
C(40)-C(39)-C(42)	108.7(3)	C(43)-C(45)-H(45C)	109.5
C(13)-C(39)-C(42)	109.6(2)	H(45A)-C(45)-H(45C)	109.5
C(41)-C(39)-C(42)	109.1(2)	H(45B)-C(45)-H(45C)	109.5
C(39)-C(40)-H(40A)	109.5	C(43)-C(46)-H(46A)	109.5
C(39)-C(40)-H(40B)	109.5	C(43)-C(46)-H(46B)	109.5
H(40A)-C(40)-H(40B)	109.5	H(46A)-C(46)-H(46B)	109.5
C(39)-C(40)-H(40C)	109.5	C(43)-C(46)-H(46C)	109.5
H(40A)-C(40)-H(40C)	109.5	H(46A)-C(46)-H(46C)	109.5
H(40B)-C(40)-H(40C)	109.5	H(46B)-C(46)-H(46C)	109.5
C(39)-C(41)-H(41A)	109.5	C(50)-C(47)-C(48)	109.0(3)
C(39)-C(41)-H(41B)	109.5	C(50)-C(47)-C(49)	107.7(3)
H(41A)-C(41)-H(41B)	109.5	C(48)-C(47)-C(49)	109.1(3)
C(39)-C(41)-H(41C)	109.5	C(50)-C(47)-C(23)	111.8(2)
H(41A)-C(41)-H(41C)	109.5	C(48)-C(47)-C(23)	109.1(2)
H(41B)-C(41)-H(41C)	109.5	C(49)-C(47)-C(23)	110.0(2)
C(39)-C(42)-H(42A)	109.5	C(47)-C(48)-H(48A)	109.5
C(39)-C(42)-H(42B)	109.5	C(47)-C(48)-H(48B)	109.5

H(48A)-C(48)-H(48B)	109.5	H(54A)-C(54)-H(54B)	109.5
C(47)-C(48)-H(48C)	109.5	C(51)-C(54)-H(54C)	109.5
H(48A)-C(48)-H(48C)	109.5	H(54A)-C(54)-H(54C)	109.5
H(48B)-C(48)-H(48C)	109.5	H(54B)-C(54)-H(54C)	109.5
C(47)-C(49)-H(49A)	109.5	C(57)-C(55)-C(58)	108.2(3)
C(47)-C(49)-H(49B)	109.5	C(57)-C(55)-C(17)	110.6(3)
H(49A)-C(49)-H(49B)	109.5	C(58)-C(55)-C(17)	111.9(3)
C(47)-C(49)-H(49C)	109.5	C(57)-C(55)-C(56)	110.5(4)
H(49A)-C(49)-H(49C)	109.5	C(58)-C(55)-C(56)	108.0(3)
H(49B)-C(49)-H(49C)	109.5	C(17)-C(55)-C(56)	107.6(3)
C(47)-C(50)-H(50A)	109.5	C(55)-C(56)-H(56A)	109.5
C(47)-C(50)-H(50B)	109.5	C(55)-C(56)-H(56B)	109.5
H(50A)-C(50)-H(50B)	109.5	H(56A)-C(56)-H(56B)	109.5
C(47)-C(50)-H(50C)	109.5	C(55)-C(56)-H(56C)	109.5
H(50A)-C(50)-H(50C)	109.5	H(56A)-C(56)-H(56C)	109.5
H(50B)-C(50)-H(50C)	109.5	H(56B)-C(56)-H(56C)	109.5
C(53)-C(51)-C(52)	108.6(2)	C(55)-C(57)-H(57A)	109.5
C(53)-C(51)-C(19)	112.1(2)	C(55)-C(57)-H(57B)	109.5
C(52)-C(51)-C(19)	109.2(2)	H(57A)-C(57)-H(57B)	109.5
C(53)-C(51)-C(54)	107.9(2)	C(55)-C(57)-H(57C)	109.5
C(52)-C(51)-C(54)	109.7(2)	H(57A)-C(57)-H(57C)	109.5
C(19)-C(51)-C(54)	109.3(2)	H(57B)-C(57)-H(57C)	109.5
C(51)-C(52)-H(52A)	109.5	C(55)-C(58)-H(58A)	109.5
C(51)-C(52)-H(52B)	109.5	C(55)-C(58)-H(58B)	109.5
H(52A)-C(52)-H(52B)	109.5	H(58A)-C(58)-H(58B)	109.5
C(51)-C(52)-H(52C)	109.5	C(55)-C(58)-H(58C)	109.5
H(52A)-C(52)-H(52C)	109.5	H(58A)-C(58)-H(58C)	109.5
H(52B)-C(52)-H(52C)	109.5	H(58B)-C(58)-H(58C)	109.5
C(51)-C(53)-H(53A)	109.5	C(57')-C(55')-C(58')	109(2)
C(51)-C(53)-H(53B)	109.5	C(57')-C(55')-C(17)	103(3)
H(53A)-C(53)-H(53B)	109.5	C(58')-C(55')-C(17)	116(3)
C(51)-C(53)-H(53C)	109.5	C(57')-C(55')-C(56')	110(2)
H(53A)-C(53)-H(53C)	109.5	C(58')-C(55')-C(56')	106(2)
H(53B)-C(53)-H(53C)	109.5	C(17)-C(55')-C(56')	113(2)
C(51)-C(54)-H(54A)	109.5	C(55')-C(56')-H(56D)	109.5
C(51)-C(54)-H(54B)	109.5	C(55')-C(56')-H(56E)	109.5

H(56D)-C(56')-H(56E)	109.5	C(62)-C(61)-H(61B)	109.2
C(55')-C(56')-H(56F)	109.5	H(61A)-C(61)-H(61B)	107.9
H(56D)-C(56')-H(56F)	109.5	O(1)-C(62)-C(61)	110.1(3)
H(56E)-C(56')-H(56F)	109.5	O(1)-C(62)-H(62A)	109.6
C(55')-C(57')-H(57D)	109.5	C(61)-C(62)-H(62A)	109.6
C(55')-C(57')-H(57E)	109.5	O(1)-C(62)-H(62B)	109.6
H(57D)-C(57')-H(57E)	109.5	C(61)-C(62)-H(62B)	109.6
C(55')-C(57')-H(57F)	109.5	H(62A)-C(62)-H(62B)	108.2
H(57D)-C(57')-H(57F)	109.5	C(63)-O(3)-C(66)	108.8(2)
H(57E)-C(57')-H(57F)	109.5	O(3)-C(63)-C(64)	110.9(3)
C(55')-C(58')-H(58D)	109.5	O(3)-C(63)-H(63A)	109.5
C(55')-C(58')-H(58E)	109.5	C(64)-C(63)-H(63A)	109.5
H(58D)-C(58')-H(58E)	109.5	O(3)-C(63)-H(63B)	109.5
C(55')-C(58')-H(58F)	109.5	C(64)-C(63)-H(63B)	109.5
H(58D)-C(58')-H(58F)	109.5	H(63A)-C(63)-H(63B)	108.1
H(58E)-C(58')-H(58F)	109.5	O(4)-C(64)-C(63)	111.2(3)
C(62)-O(1)-C(59)	108.9(3)	O(4)-C(64)-H(64A)	109.4
O(1)-C(59)-C(60)	110.3(3)	C(63)-C(64)-H(64A)	109.4
O(1)-C(59)-H(59A)	109.6	O(4)-C(64)-H(64B)	109.4
C(60)-C(59)-H(59A)	109.6	C(63)-C(64)-H(64B)	109.4
O(1)-C(59)-H(59B)	109.6	H(64A)-C(64)-H(64B)	108.0
C(60)-C(59)-H(59B)	109.6	C(65)-O(4)-C(64)	109.3(2)
H(59A)-C(59)-H(59B)	108.1	O(4)-C(65)-C(66)	110.9(3)
O(2)-C(60)-C(59)	111.3(3)	O(4)-C(65)-H(65A)	109.5
O(2)-C(60)-H(60A)	109.4	C(66)-C(65)-H(65A)	109.5
C(59)-C(60)-H(60A)	109.4	O(4)-C(65)-H(65B)	109.5
O(2)-C(60)-H(60B)	109.4	C(66)-C(65)-H(65B)	109.5
C(59)-C(60)-H(60B)	109.4	H(65A)-C(65)-H(65B)	108.0
H(60A)-C(60)-H(60B)	108.0	O(3)-C(66)-C(65)	110.5(3)
C(61)-O(2)-C(60)	108.9(3)	O(3)-C(66)-H(66A)	109.5
O(2)-C(61)-C(62)	111.9(3)	C(65)-C(66)-H(66A)	109.5
O(2)-C(61)-H(61A)	109.2	O(3)-C(66)-H(66B)	109.5
C(62)-C(61)-H(61A)	109.2	C(65)-C(66)-H(66B)	109.5
O(2)-C(61)-H(61B)	109.2	H(66A)-C(66)-H(66B)	108.1

Table S10. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk04. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12} ]$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Fe1	23(1)	21(1)	19(1)	6(1)	10(1)	5(1)
Cl1	24(1)	39(1)	40(1)	15(1)	14(1)	6(1)
Cl2	48(1)	35(1)	17(1)	0(1)	7(1)	10(1)
P1	18(1)	14(1)	17(1)	1(1)	1(1)	0(1)
P2	21(1)	14(1)	14(1)	2(1)	7(1)	1(1)
C1	25(1)	19(1)	16(1)	-1(1)	9(1)	-1(1)
C2	22(1)	19(1)	15(1)	1(1)	3(1)	0(1)
C3	21(1)	19(1)	17(1)	-1(1)	6(1)	-3(1)
C4	20(1)	21(1)	17(1)	1(1)	4(1)	1(1)
C5	21(1)	18(1)	18(1)	1(1)	5(1)	2(1)
C6	23(1)	21(1)	18(1)	-2(1)	7(1)	-4(1)
C7	19(1)	23(1)	18(1)	2(1)	4(1)	0(1)
C8	16(1)	19(1)	17(1)	3(1)	0(1)	2(1)
C9	17(1)	15(1)	18(1)	0(1)	0(1)	-2(1)
C10	22(1)	19(1)	18(1)	1(1)	6(1)	1(1)
C11	25(1)	19(1)	14(1)	-1(1)	1(1)	0(1)
C12	17(1)	23(1)	21(2)	-2(1)	0(1)	2(1)
C13	20(1)	19(1)	19(1)	0(1)	4(1)	-2(1)
C14	20(1)	17(1)	14(1)	2(1)	3(1)	-4(1)
C15	18(1)	16(1)	16(1)	1(1)	4(1)	-3(1)
C16	26(1)	21(1)	15(1)	5(1)	6(1)	1(1)
C17	23(1)	28(2)	21(2)	3(1)	9(1)	3(1)
C18	21(1)	21(1)	19(1)	3(1)	3(1)	0(1)
C19	23(1)	17(1)	16(1)	0(1)	4(1)	-4(1)
C20	22(1)	15(1)	17(1)	-2(1)	5(1)	-3(1)
C21	22(1)	18(1)	12(1)	-1(1)	7(1)	2(1)
C22	21(1)	18(1)	14(1)	2(1)	7(1)	5(1)
C23	27(1)	19(1)	14(1)	-1(1)	10(1)	0(1)
C24	22(1)	25(1)	17(1)	-4(1)	7(1)	-2(1)
C25	20(1)	28(2)	11(1)	-5(1)	5(1)	4(1)
C26	27(1)	20(1)	11(1)	1(1)	6(1)	6(1)

C27	18(1)	21(1)	25(2)	5(1)	-1(1)	-3(1)
C28	34(2)	37(2)	111(4)	23(2)	-26(2)	-14(2)
C29	29(2)	73(3)	24(2)	-6(2)	-1(1)	3(2)
C30	19(1)	59(2)	31(2)	-2(2)	1(1)	5(1)
C31	22(1)	19(1)	26(2)	0(1)	3(1)	2(1)
C32	34(2)	20(2)	42(2)	6(1)	-4(2)	0(1)
C33	45(2)	24(2)	22(2)	3(1)	-4(1)	3(1)
C34	38(2)	39(2)	51(2)	13(2)	20(2)	18(2)
C35	31(2)	30(2)	15(1)	1(1)	-1(1)	6(1)
C36	53(2)	49(2)	20(2)	-5(2)	-6(2)	25(2)
C37	60(2)	52(2)	20(2)	11(2)	4(2)	-9(2)
C38	50(2)	31(2)	20(2)	-2(1)	-3(1)	10(2)
C39	22(1)	26(2)	24(2)	-1(1)	9(1)	0(1)
C40	35(2)	48(2)	26(2)	-2(2)	14(1)	8(2)
C41	34(2)	30(2)	34(2)	-2(1)	16(1)	3(1)
C42	30(2)	33(2)	46(2)	-5(2)	19(2)	-2(1)
C43	20(1)	34(2)	18(1)	-1(1)	2(1)	3(1)
C44	31(2)	40(2)	50(2)	-17(2)	-7(2)	15(1)
C45	24(2)	46(2)	43(2)	-14(2)	-1(1)	0(1)
C46	36(2)	69(3)	29(2)	12(2)	-4(2)	2(2)
C47	28(1)	16(1)	30(2)	2(1)	9(1)	-2(1)
C48	79(3)	19(2)	48(2)	-4(2)	36(2)	-5(2)
C49	39(2)	26(2)	30(2)	4(1)	14(1)	-4(1)
C50	37(2)	29(2)	71(3)	26(2)	10(2)	1(1)
C51	31(2)	22(1)	15(1)	3(1)	3(1)	2(1)
C52	38(2)	31(2)	17(2)	1(1)	-6(1)	1(1)
C53	42(2)	30(2)	16(2)	3(1)	9(1)	5(1)
C54	39(2)	25(2)	24(2)	4(1)	12(1)	5(1)
C55	29(2)	45(2)	22(2)	11(2)	12(2)	17(2)
C56	50(3)	64(3)	65(5)	44(3)	43(3)	32(3)
C57	49(4)	93(4)	22(2)	-16(2)	3(2)	37(3)
C58	32(2)	40(2)	25(3)	6(2)	11(2)	13(2)
C55'	29(2)	45(2)	22(2)	11(2)	12(2)	17(2)
C56'	50(3)	64(3)	65(5)	44(3)	43(3)	32(3)
C57'	49(4)	93(4)	22(2)	-16(2)	3(2)	37(3)
C58'	32(2)	40(2)	25(3)	6(2)	11(2)	13(2)

O1	56(2)	57(2)	44(2)	-4(1)	18(1)	-12(1)
C59	65(3)	50(2)	36(2)	15(2)	22(2)	8(2)
C60	50(2)	76(3)	42(2)	-13(2)	22(2)	-7(2)
O2	42(2)	116(3)	44(2)	3(2)	12(1)	6(2)
C61	39(2)	86(3)	32(2)	14(2)	11(2)	11(2)
C62	74(3)	65(3)	34(2)	-9(2)	24(2)	9(2)
O3	28(1)	36(1)	33(1)	7(1)	-2(1)	5(1)
C63	23(2)	47(2)	30(2)	10(2)	0(1)	-3(1)
C64	34(2)	53(2)	31(2)	3(2)	2(2)	-6(2)
O4	28(1)	50(2)	43(2)	9(1)	-5(1)	6(1)
C65	34(2)	56(2)	43(2)	3(2)	4(2)	10(2)
C66	36(2)	44(2)	42(2)	-6(2)	-1(2)	8(2)

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Table S11. Hydrogen coordinates ( $x \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk04.

	x	y	z	U(eq)
H1A	6239	2314	7140	23
H1B	7143	2176	7850	23
H2A	8044	2803	7559	23
H2B	7003	3005	7613	23
H4	6583	3955	5719	23
H6	8896	4773	6609	24
H8	8995	3397	7144	21
H10	6096	3091	4708	23
H12	3391	3439	4873	25
H14	5427	3209	6915	21
H16	8994	1514	6130	24
H18	10525	855	8099	25
H20	8177	1610	8278	22
H22	7209	942	7006	21
H24	4417	646	5983	25
H26	5489	1920	5691	23
H28A	10121	4860	7652	101
H28B	10585	4693	6914	101
H28C	11186	4639	7829	101
H29A	9608	4264	8561	65
H29B	10701	4078	8742	65
H29C	9822	3726	8429	65
H30A	11446	3834	7596	55
H30B	10812	3846	6688	55
H30C	10564	3478	7327	55
H32A	8194	5236	5439	51
H32B	7921	5366	6285	51
H32C	7249	5541	5449	51
H33A	7213	4665	4513	48
H33B	6310	5003	4503	48

H33C	6239	4464	4721	48
H34A	6455	5020	6645	62
H34B	5807	4658	6037	62
H34C	5822	5197	5795	62
H36A	2937	3381	3600	64
H36B	3287	3551	2806	64
H36C	3477	3871	3601	64
H37A	5818	3424	3546	68
H37B	5252	3898	3629	68
H37C	5005	3608	2799	68
H38A	3840	2647	3526	53
H38B	4981	2657	3565	53
H38C	4240	2834	2767	53
H40A	4409	3668	7520	53
H40B	4216	3119	7522	53
H40C	3394	3475	7655	53
H41A	3618	4155	6351	48
H41B	2613	3995	6557	48
H41C	2787	3934	5656	48
H42A	2958	2763	6379	53
H42B	2405	3091	5660	53
H42C	2197	3141	6552	53
H44A	3938	2111	5820	64
H44B	3306	1747	6205	64
H44C	2854	1993	5356	64
H45A	3293	823	4815	58
H45B	2450	1199	4781	58
H45C	2957	966	5628	58
H46A	4296	1378	4191	70
H46B	4360	1909	4486	70
H46C	3334	1688	4069	70
H48A	5143	-82	5833	68
H48B	5854	-447	6382	68
H48C	6278	-74	5845	68
H49A	4558	173	7074	46
H49B	5330	333	7868	46

H49C	5274	-201	7592	46
H50A	7456	197	7098	69
H50B	7018	-188	7602	69
H50C	7062	345	7883	69
H52A	10678	1163	10241	46
H52B	10558	1600	9639	46
H52C	11050	1131	9411	46
H53A	8150	1154	9389	43
H53B	8778	1620	9594	43
H53C	8941	1195	10222	43
H54A	8889	430	9022	43
H54B	9642	457	9879	43
H54C	10028	408	9058	43
H56A	10470	1610	5833	83
H56B	11453	1330	5848	83
H56C	11320	1615	6632	83
H57A	9473	890	5457	84
H57B	9701	429	5997	84
H57C	10430	594	5447	84
H58A	11745	870	7422	47
H58B	11818	610	6599	47
H58C	11125	409	7152	47
H56D	10876	1768	6406	83
H56E	11709	1463	6151	83
H56F	11785	1598	7083	83
H57D	9992	1073	5521	84
H57E	9946	582	5958	84
H57F	10897	725	5645	84
H58D	11707	841	7759	47
H58E	12127	736	6969	47
H58F	11280	418	7171	47
H59A	6859	3806	9614	59
H59B	6068	4147	9854	59
H60A	6925	4793	9562	65
H60B	7606	4475	10233	65
H61A	7896	4419	7981	62

H61B	7101	4760	8214	62
H62A	6354	4096	7582	67
H62B	7024	3773	8250	67
H63A	9735	2315	8923	41
H63B	9468	2848	9052	41
H64A	11109	3055	9319	48
H64B	10956	2647	9927	48
H65A	12043	2334	8035	54
H65B	11747	2862	8168	54
H66A	10552	2502	7167	51
H66B	10404	2110	7805	51

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Table S12. Torsion angles [°] for neijk04.

C15-P2-C1-C2	95.7(2)	C9-C10-C11-C35	179.4(2)
C21-P2-C1-C2	-155.27(19)	C10-C11-C12-C13	1.5(4)
Fe1-P2-C1-C2	-27.0(2)	C35-C11-C12-C13	179.8(3)
P2-C1-C2-P1	50.1(2)	C11-C12-C13-C14	0.1(4)
C9-P1-C2-C1	70.6(2)	C11-C12-C13-C39	179.2(3)
C3-P1-C2-C1	-178.80(18)	C12-C13-C14-C9	-1.0(4)
Fe1-P1-C2-C1	-48.05(19)	C39-C13-C14-C9	180.0(2)
C9-P1-C3-C8	165.7(2)	C10-C9-C14-C13	0.3(4)
C2-P1-C3-C8	51.9(2)	P1-C9-C14-C13	175.2(2)
Fe1-P1-C3-C8	-66.8(2)	C21-P2-C15-C16	95.6(2)
C9-P1-C3-C4	-17.2(3)	C1-P2-C15-C16	-157.3(2)
C2-P1-C3-C4	-131.0(2)	Fe1-P2-C15-C16	-38.3(2)
Fe1-P1-C3-C4	110.3(2)	C21-P2-C15-C20	-79.0(2)
C8-C3-C4-C5	0.9(4)	C1-P2-C15-C20	28.1(3)
P1-C3-C4-C5	-176.2(2)	Fe1-P2-C15-C20	147.11(19)
C3-C4-C5-C6	-0.1(4)	C20-C15-C16-C17	0.3(4)
C3-C4-C5-C31	-179.6(2)	P2-C15-C16-C17	-174.5(2)
C4-C5-C6-C7	-1.2(4)	C15-C16-C17-C18	0.3(4)
C31-C5-C6-C7	178.3(3)	C15-C16-C17-C55	-179.3(4)
C5-C6-C7-C8	1.7(4)	C15-C16-C17-C55'	-161(2)
C5-C6-C7-C27	-176.4(3)	C16-C17-C18-C19	-0.6(4)
C4-C3-C8-C7	-0.4(4)	C55-C17-C18-C19	178.9(4)
P1-C3-C8-C7	176.7(2)	C55'-C17-C18-C19	163.0(17)
C6-C7-C8-C3	-0.8(4)	C17-C18-C19-C20	0.4(4)
C27-C7-C8-C3	177.3(2)	C17-C18-C19-C51	179.7(2)
C3-P1-C9-C10	90.2(2)	C18-C19-C20-C15	0.2(4)
C2-P1-C9-C10	-159.47(19)	C51-C19-C20-C15	-179.2(2)
Fe1-P1-C9-C10	-44.6(2)	C16-C15-C20-C19	-0.5(4)
C3-P1-C9-C14	-84.9(2)	P2-C15-C20-C19	173.9(2)
C2-P1-C9-C14	25.4(3)	C15-P2-C21-C26	-176.4(2)
Fe1-P1-C9-C14	140.2(2)	C1-P2-C21-C26	70.5(2)
C14-C9-C10-C11	1.4(4)	Fe1-P2-C21-C26	-47.6(2)
P1-C9-C10-C11	-174.0(2)	C15-P2-C21-C22	5.9(2)
C9-C10-C11-C12	-2.2(4)	C1-P2-C21-C22	-107.2(2)

Fe1-P2-C21-C22	134.70(19)	C12-C13-C39-C42	62.8(3)
C26-C21-C22-C23	-0.5(4)	C24-C25-C43-C44	116.8(3)
P2-C21-C22-C23	177.1(2)	C26-C25-C43-C44	-63.2(3)
C21-C22-C23-C24	-0.3(4)	C24-C25-C43-C46	-121.2(3)
C21-C22-C23-C47	-180.0(2)	C26-C25-C43-C46	58.8(3)
C22-C23-C24-C25	0.5(4)	C24-C25-C43-C45	-3.3(4)
C47-C23-C24-C25	-179.8(2)	C26-C25-C43-C45	176.7(2)
C23-C24-C25-C26	0.1(4)	C22-C23-C47-C50	3.3(4)
C23-C24-C25-C43	-180.0(2)	C24-C23-C47-C50	-176.4(3)
C22-C21-C26-C25	1.2(4)	C22-C23-C47-C48	-117.4(3)
P2-C21-C26-C25	-176.6(2)	C24-C23-C47-C48	62.9(3)
C24-C25-C26-C21	-1.0(4)	C22-C23-C47-C49	122.9(3)
C43-C25-C26-C21	179.1(2)	C24-C23-C47-C49	-56.8(3)
C6-C7-C27-C28	-8.2(4)	C20-C19-C51-C53	1.0(4)
C8-C7-C27-C28	173.6(3)	C18-C19-C51-C53	-178.4(2)
C6-C7-C27-C29	113.2(3)	C20-C19-C51-C52	-119.5(3)
C8-C7-C27-C29	-65.0(3)	C18-C19-C51-C52	61.2(3)
C6-C7-C27-C30	-128.1(3)	C20-C19-C51-C54	120.6(3)
C8-C7-C27-C30	53.8(3)	C18-C19-C51-C54	-58.8(3)
C4-C5-C31-C32	-172.9(3)	C16-C17-C55-C57	-60.4(4)
C6-C5-C31-C32	7.6(4)	C18-C17-C55-C57	120.1(4)
C4-C5-C31-C34	66.7(3)	C55'-C17-C55-C57	176(5)
C6-C5-C31-C34	-112.7(3)	C16-C17-C55-C58	178.9(3)
C4-C5-C31-C33	-52.9(3)	C18-C17-C55-C58	-0.6(5)
C6-C5-C31-C33	127.7(3)	C55'-C17-C55-C58	55(4)
C12-C11-C35-C38	-106.0(3)	C16-C17-C55-C56	60.4(4)
C10-C11-C35-C38	72.3(3)	C18-C17-C55-C56	-119.1(4)
C12-C11-C35-C37	134.5(3)	C55'-C17-C55-C56	-64(4)
C10-C11-C35-C37	-47.2(4)	C16-C17-C55'-C57'	-61(2)
C12-C11-C35-C36	14.3(4)	C18-C17-C55'-C57'	138(2)
C10-C11-C35-C36	-167.4(3)	C55-C17-C55'-C57'	5(4)
C14-C13-C39-C40	2.7(4)	C16-C17-C55'-C58'	-179.6(19)
C12-C13-C39-C40	-176.3(3)	C18-C17-C55'-C58'	19(3)
C14-C13-C39-C41	122.4(3)	C55-C17-C55'-C58'	-114(5)
C12-C13-C39-C41	-56.5(3)	C16-C17-C55'-C56'	58(3)
C14-C13-C39-C42	-118.2(3)	C18-C17-C55'-C56'	-104(2)

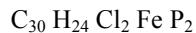
C55-C17-C55'-C56'	124(6)	C66-O3-C63-C64	57.3(4)
C62-O1-C59-C60	58.2(4)	O3-C63-C64-O4	-57.1(4)
O1-C59-C60-O2	-59.0(5)	C63-C64-O4-C65	56.5(4)
C59-C60-O2-C61	57.4(5)	C64-O4-C65-C66	-58.0(4)
C60-O2-C61-C62	-57.4(5)	C63-O3-C66-C65	-58.7(4)
C59-O1-C62-C61	-57.7(4)	O4-C65-C66-O3	60.3(4)
O2-C61-C62-O1	58.6(4)		

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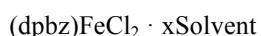
### 3.3 FeCl<sub>2</sub>(dpbz)

REFERENCE NUMBER: neijk31

#### CRYSTAL STRUCTURE REPORT



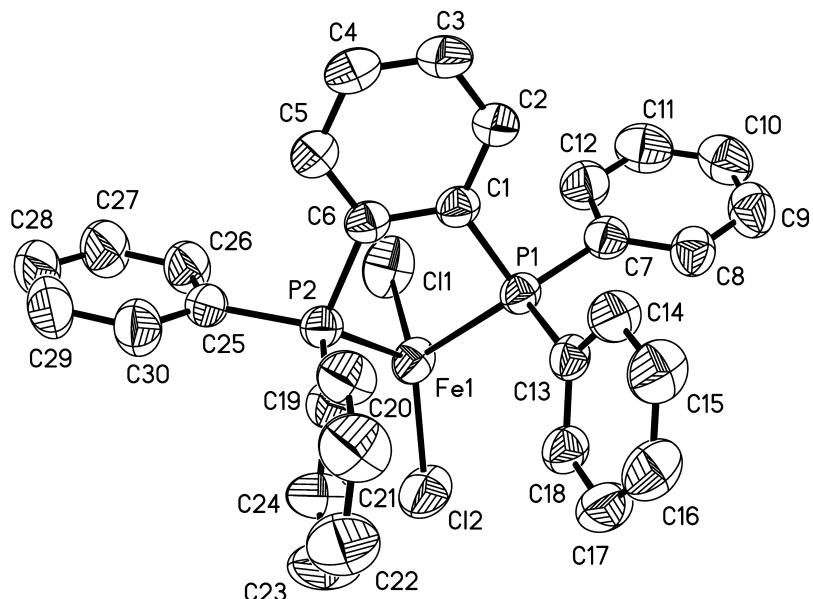
or



Report prepared for:

J. Bailey, J. Kneebone, Prof. M. Neidig

September 28, 2014



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### Data collection

A crystal ( $0.24 \times 0.20 \times 0.12 \text{ mm}^3$ ) was placed onto the tip of a thin glass optical fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at  $173(2) \text{ K}$ .<sup>1</sup> A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 4.02 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with  $0.50^\circ$  steps in  $\omega$  at six different  $\phi$  settings and a detector position of  $-38^\circ$  in  $2\theta$ . The intensity data were corrected for absorption.<sup>2</sup> Final cell constants were calculated from the xyz centroids of 4091 strong reflections from the actual data collection after integration.<sup>3</sup> See Table 1 for additional crystal and refinement information.

### Structure solution and refinement

The structure was solved using SIR2011<sup>4</sup> and refined using SHELXL-2014/7.<sup>5</sup> The space group  $P-1$  was determined based on intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Highly disordered solvent (perhaps toluene) was found in a pocket located at a crystallographic inversion center. Reflection contributions from the disordered solvent were fixed and added to the calculated structure factors using the SQUEEZE routine of program Platon,<sup>6</sup> which determined there to be 59 electrons in  $205 \text{ \AA}^3$  that were accounted for per unit cell. Because the exact identity and amount of disordered solvent is not known, no disordered solvent was included in the atom list and molecular formula. Thus all calculations that derive from the molecular formula (e.g., F(000), density, molecular weight, etc.) are known to be incorrect.

The final full matrix least squares refinement converged to  $R1 = 0.0405 (F^2, I > 2\sigma(I))$  and  $wR2 = 0.1096 (F^2, \text{all data})$ .

### Structure description

The structure is the one suggested. The asymmetric unit contains one iron complex in a general position and one-half of a solvent molecule (see above) on a crystallographic inversion center.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

<sup>1</sup> *APEX3*, version 2015.5-2; Bruker AXS: Madison, WI, 2015.

<sup>2</sup> Sheldrick, G. M. *SADABS*, version 2014/5; *J. Appl. Cryst.* **2015**, *48*, 3-10.

<sup>3</sup> *SAINT*, version 8.34A; Bruker AXS: Madison, WI, 2013.

<sup>4</sup> Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011*, version 1.0; *J. Appl. Cryst.* **2012**, *45*, 357-361.

<sup>5</sup> Sheldrick, G. M. *SHELXL-2014/7*; *Acta. Cryst.* **2015**, C71, 3-8.

<sup>6</sup> Spek, A. L. *PLATON*, version 07052015; *Acta. Cryst.* **2015**, C71, 9-18.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where  $m$  = number of reflections and  $n$  = number of parameters

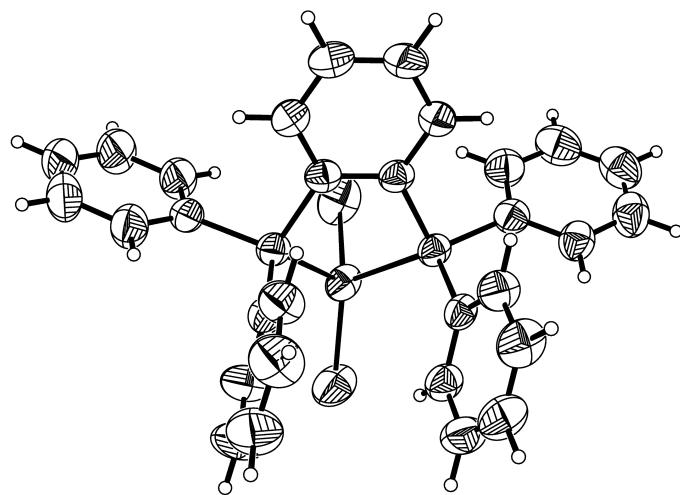


Table S13. Crystal data and structure refinement for neijk31.

Identification code	neijk31		
Empirical formula	C30 H24 Cl2 Fe P2		
Formula weight	573.18		
Temperature	173(2) K		
Wavelength	0.71073 Å		
Crystal system	triclinic		
Space group	<i>P</i> -1		
Unit cell dimensions	<i>a</i> = 9.381(2) Å	<i>α</i> = 82.096(5)°	
	<i>b</i> = 10.138(2) Å	<i>β</i> = 81.479(5)°	
	<i>c</i> = 17.591(4) Å	<i>γ</i> = 68.716(5)°	
Volume	1535.4(6) Å <sup>3</sup>		
<i>Z</i>	2		
Density (calculated)	1.240 Mg/m <sup>3</sup>		
Absorption coefficient	0.785 mm <sup>-1</sup>		
<i>F</i> (000)	588		
Crystal color, morphology	colorless, block		
Crystal size	0.24 x 0.20 x 0.12 mm <sup>3</sup>		
Theta range for data collection	2.343 to 28.348°		
Index ranges	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -23 ≤ <i>l</i> ≤ 23		
Reflections collected	32606		
Independent reflections	7663 [ <i>R</i> (int) = 0.0433]		
Observed reflections	5295		
Completeness to theta = 28.283°	99.9%		
Absorption correction	Multi-scan		
Max. and min. transmission	0.7457 and 0.6560		
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>		
Data / restraints / parameters	7663 / 0 / 316		
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.012		
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> 1 = 0.0405, <i>wR</i> 2 = 0.0969		
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0657, <i>wR</i> 2 = 0.1096		
Largest diff. peak and hole	0.469 and -0.289 e.Å <sup>-3</sup>		

Table S14. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk31.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
Fe1	-969(1)	7580(1)	2110(1)	53(1)
Cl1	-2145(1)	9477(1)	1342(1)	82(1)
Cl2	-2126(1)	6257(1)	2870(1)	90(1)
P1	1417(1)	6412(1)	1320(1)	43(1)
P2	808(1)	8251(1)	2714(1)	45(1)
C1	2439(2)	7655(2)	1271(1)	44(1)
C2	3465(3)	7816(2)	643(1)	58(1)
C3	4247(3)	8731(3)	641(2)	70(1)
C4	3999(3)	9524(3)	1255(2)	69(1)
C5	2965(3)	9395(2)	1879(1)	56(1)
C6	2179(2)	8464(2)	1900(1)	44(1)
C7	1395(2)	6181(2)	317(1)	50(1)
C8	2099(3)	4881(3)	9(1)	58(1)
C9	1977(3)	4773(3)	-754(2)	72(1)
C10	1164(3)	5919(4)	-1201(2)	76(1)
C11	445(3)	7204(3)	-901(2)	80(1)
C12	557(3)	7344(3)	-144(2)	68(1)
C13	2732(2)	4755(2)	1733(1)	44(1)
C14	4294(2)	4268(2)	1480(1)	58(1)
C15	5255(3)	3008(3)	1804(2)	71(1)
C16	4695(3)	2239(3)	2387(2)	73(1)
C17	3158(3)	2712(3)	2653(2)	68(1)
C18	2176(3)	3967(2)	2321(1)	54(1)
C19	1939(3)	6869(2)	3380(1)	50(1)
C20	3524(3)	6395(3)	3313(1)	64(1)
C21	4316(4)	5312(3)	3822(2)	86(1)
C22	3554(4)	4706(3)	4395(2)	93(1)
C23	1985(4)	5160(3)	4471(2)	92(1)
C24	1168(3)	6244(3)	3960(2)	71(1)
C25	202(3)	9891(2)	3180(1)	51(1)
C26	-929(3)	11056(3)	2871(1)	68(1)

C27	-1419(4)	12339(3)	3191(2)	85(1)
C28	-798(4)	12448(3)	3824(2)	89(1)
C29	309(4)	11304(3)	4141(2)	87(1)
C30	820(3)	10009(3)	3823(1)	70(1)

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Table S15. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for neijk31.

Fe(1)-Cl(2)	2.2132(8)	C(14)-H(14)	0.9500
Fe(1)-Cl(1)	2.2190(8)	C(15)-C(16)	1.362(4)
Fe(1)-P(2)	2.4330(7)	C(15)-H(15)	0.9500
Fe(1)-P(1)	2.4389(7)	C(16)-C(17)	1.374(4)
P(1)-C(13)	1.816(2)	C(16)-H(16)	0.9500
P(1)-C(7)	1.816(2)	C(17)-C(18)	1.382(3)
P(1)-C(1)	1.828(2)	C(17)-H(17)	0.9500
P(2)-C(19)	1.816(2)	C(18)-H(18)	0.9500
P(2)-C(25)	1.819(2)	C(19)-C(20)	1.379(3)
P(2)-C(6)	1.822(2)	C(19)-C(24)	1.380(3)
C(1)-C(2)	1.387(3)	C(20)-C(21)	1.377(3)
C(1)-C(6)	1.407(3)	C(20)-H(20)	0.9500
C(2)-C(3)	1.376(3)	C(21)-C(22)	1.355(4)
C(2)-H(2)	0.9500	C(21)-H(21)	0.9500
C(3)-C(4)	1.376(4)	C(22)-C(23)	1.366(5)
C(3)-H(3)	0.9500	C(22)-H(22)	0.9500
C(4)-C(5)	1.378(3)	C(23)-C(24)	1.388(4)
C(4)-H(4)	0.9500	C(23)-H(23)	0.9500
C(5)-C(6)	1.387(3)	C(24)-H(24)	0.9500
C(5)-H(5)	0.9500	C(25)-C(26)	1.379(3)
C(7)-C(12)	1.386(3)	C(25)-C(30)	1.382(3)
C(7)-C(8)	1.388(3)	C(26)-C(27)	1.383(4)
C(8)-C(9)	1.385(3)	C(26)-H(26)	0.9500
C(8)-H(8)	0.9500	C(27)-C(28)	1.366(4)
C(9)-C(10)	1.354(4)	C(27)-H(27)	0.9500
C(9)-H(9)	0.9500	C(28)-C(29)	1.361(4)
C(10)-C(11)	1.370(4)	C(28)-H(28)	0.9500
C(10)-H(10)	0.9500	C(29)-C(30)	1.391(4)
C(11)-C(12)	1.381(4)	C(29)-H(29)	0.9500
C(11)-H(11)	0.9500	C(30)-H(30)	0.9500
C(12)-H(12)	0.9500	Cl(2)-Fe(1)-Cl(1)	124.85(4)
C(13)-C(18)	1.377(3)	Cl(2)-Fe(1)-P(2)	115.16(3)
C(13)-C(14)	1.390(3)	Cl(1)-Fe(1)-P(2)	105.32(3)
C(14)-C(15)	1.373(3)	Cl(2)-Fe(1)-P(1)	119.01(3)

Cl(1)-Fe(1)-P(1)	102.85(3)	C(9)-C(8)-H(8)	120.1
P(2)-Fe(1)-P(1)	80.38(3)	C(7)-C(8)-H(8)	120.1
C(13)-P(1)-C(7)	106.69(10)	C(10)-C(9)-C(8)	120.8(3)
C(13)-P(1)-C(1)	103.67(9)	C(10)-C(9)-H(9)	119.6
C(7)-P(1)-C(1)	104.07(10)	C(8)-C(9)-H(9)	119.6
C(13)-P(1)-Fe(1)	117.38(7)	C(9)-C(10)-C(11)	120.1(3)
C(7)-P(1)-Fe(1)	120.57(7)	C(9)-C(10)-H(10)	120.0
C(1)-P(1)-Fe(1)	102.08(7)	C(11)-C(10)-H(10)	120.0
C(19)-P(2)-C(25)	105.84(10)	C(10)-C(11)-C(12)	120.3(3)
C(19)-P(2)-C(6)	105.37(10)	C(10)-C(11)-H(11)	119.8
C(25)-P(2)-C(6)	104.69(10)	C(12)-C(11)-H(11)	119.8
C(19)-P(2)-Fe(1)	114.56(8)	C(11)-C(12)-C(7)	120.1(2)
C(25)-P(2)-Fe(1)	122.11(8)	C(11)-C(12)-H(12)	120.0
C(6)-P(2)-Fe(1)	102.56(7)	C(7)-C(12)-H(12)	120.0
C(2)-C(1)-C(6)	119.3(2)	C(18)-C(13)-C(14)	118.9(2)
C(2)-C(1)-P(1)	122.38(17)	C(18)-C(13)-P(1)	119.33(15)
C(6)-C(1)-P(1)	118.32(15)	C(14)-C(13)-P(1)	121.78(17)
C(3)-C(2)-C(1)	120.4(2)	C(15)-C(14)-C(13)	120.2(2)
C(3)-C(2)-H(2)	119.8	C(15)-C(14)-H(14)	119.9
C(1)-C(2)-H(2)	119.8	C(13)-C(14)-H(14)	119.9
C(4)-C(3)-C(2)	120.6(2)	C(16)-C(15)-C(14)	120.4(2)
C(4)-C(3)-H(3)	119.7	C(16)-C(15)-H(15)	119.8
C(2)-C(3)-H(3)	119.7	C(14)-C(15)-H(15)	119.8
C(3)-C(4)-C(5)	119.8(2)	C(15)-C(16)-C(17)	120.2(2)
C(3)-C(4)-H(4)	120.1	C(15)-C(16)-H(16)	119.9
C(5)-C(4)-H(4)	120.1	C(17)-C(16)-H(16)	119.9
C(4)-C(5)-C(6)	120.8(2)	C(16)-C(17)-C(18)	119.8(2)
C(4)-C(5)-H(5)	119.6	C(16)-C(17)-H(17)	120.1
C(6)-C(5)-H(5)	119.6	C(18)-C(17)-H(17)	120.1
C(5)-C(6)-C(1)	119.11(19)	C(13)-C(18)-C(17)	120.4(2)
C(5)-C(6)-P(2)	122.39(17)	C(13)-C(18)-H(18)	119.8
C(1)-C(6)-P(2)	118.49(15)	C(17)-C(18)-H(18)	119.8
C(12)-C(7)-C(8)	119.0(2)	C(20)-C(19)-C(24)	119.2(2)
C(12)-C(7)-P(1)	117.91(17)	C(20)-C(19)-P(2)	122.83(18)
C(8)-C(7)-P(1)	122.99(18)	C(24)-C(19)-P(2)	117.99(18)
C(9)-C(8)-C(7)	119.8(2)	C(21)-C(20)-C(19)	120.0(3)

C(21)-C(20)-H(20)	120.0	C(30)-C(25)-P(2)	122.97(17)
C(19)-C(20)-H(20)	120.0	C(25)-C(26)-C(27)	120.3(3)
C(22)-C(21)-C(20)	120.7(3)	C(25)-C(26)-H(26)	119.8
C(22)-C(21)-H(21)	119.6	C(27)-C(26)-H(26)	119.8
C(20)-C(21)-H(21)	119.6	C(28)-C(27)-C(26)	119.8(3)
C(21)-C(22)-C(23)	120.3(3)	C(28)-C(27)-H(27)	120.1
C(21)-C(22)-H(22)	119.9	C(26)-C(27)-H(27)	120.1
C(23)-C(22)-H(22)	119.9	C(29)-C(28)-C(27)	120.6(2)
C(22)-C(23)-C(24)	119.8(3)	C(29)-C(28)-H(28)	119.7
C(22)-C(23)-H(23)	120.1	C(27)-C(28)-H(28)	119.7
C(24)-C(23)-H(23)	120.1	C(28)-C(29)-C(30)	120.2(3)
C(19)-C(24)-C(23)	120.1(3)	C(28)-C(29)-H(29)	119.9
C(19)-C(24)-H(24)	120.0	C(30)-C(29)-H(29)	119.9
C(23)-C(24)-H(24)	120.0	C(25)-C(30)-C(29)	119.6(3)
C(26)-C(25)-C(30)	119.4(2)	C(25)-C(30)-H(30)	120.2
C(26)-C(25)-P(2)	117.60(18)	C(29)-C(30)-H(30)	120.2

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Table S16. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk31. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12} ]$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Fe1	36(1)	45(1)	74(1)	-13(1)	4(1)	-11(1)
Cl1	59(1)	63(1)	109(1)	-12(1)	-28(1)	6(1)
Cl2	75(1)	74(1)	124(1)	-27(1)	39(1)	-41(1)
P1	37(1)	37(1)	53(1)	-6(1)	1(1)	-11(1)
P2	43(1)	39(1)	48(1)	-4(1)	0(1)	-11(1)
C1	39(1)	37(1)	52(1)	-2(1)	0(1)	-12(1)
C2	64(1)	54(1)	57(1)	-9(1)	11(1)	-27(1)
C3	72(2)	68(2)	72(2)	-5(1)	18(1)	-39(1)
C4	76(2)	69(2)	76(2)	-5(1)	3(1)	-47(1)
C5	64(1)	55(1)	58(1)	-7(1)	-3(1)	-30(1)
C6	40(1)	41(1)	49(1)	0(1)	-5(1)	-13(1)
C7	44(1)	52(1)	57(1)	-6(1)	-1(1)	-20(1)
C8	54(1)	58(1)	64(1)	-13(1)	-6(1)	-21(1)
C9	70(2)	82(2)	73(2)	-28(2)	-1(1)	-34(2)
C10	80(2)	106(2)	58(2)	-10(2)	-8(1)	-49(2)
C11	82(2)	91(2)	65(2)	9(2)	-18(1)	-32(2)
C12	72(2)	61(2)	66(2)	-1(1)	-12(1)	-18(1)
C13	41(1)	38(1)	53(1)	-10(1)	-1(1)	-11(1)
C14	44(1)	52(1)	72(2)	-5(1)	2(1)	-11(1)
C15	42(1)	59(2)	97(2)	-6(1)	-4(1)	-1(1)
C16	65(2)	47(1)	92(2)	2(1)	-17(1)	-2(1)
C17	73(2)	48(1)	73(2)	6(1)	-5(1)	-16(1)
C18	48(1)	44(1)	64(1)	-7(1)	2(1)	-13(1)
C19	54(1)	42(1)	49(1)	-6(1)	-3(1)	-12(1)
C20	56(1)	63(2)	62(1)	2(1)	-6(1)	-10(1)
C21	70(2)	80(2)	85(2)	6(2)	-18(2)	0(2)
C22	107(3)	70(2)	82(2)	19(2)	-31(2)	-9(2)
C23	110(3)	80(2)	76(2)	27(2)	-9(2)	-34(2)
C24	67(2)	69(2)	68(2)	14(1)	0(1)	-25(1)
C25	58(1)	40(1)	49(1)	-6(1)	3(1)	-13(1)
C26	82(2)	49(1)	61(1)	-6(1)	-9(1)	-6(1)

C27	112(2)	47(1)	73(2)	-9(1)	-6(2)	0(2)
C28	136(3)	49(2)	70(2)	-19(1)	10(2)	-19(2)
C29	128(3)	72(2)	60(2)	-20(1)	-11(2)	-28(2)
C30	89(2)	56(1)	61(1)	-10(1)	-13(1)	-15(1)

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Table S17. Hydrogen coordinates ( $x \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk31.

	x	y	z	U(eq)
H2	3629	7290	211	70
H3	4965	8817	213	83
H4	4539	10158	1249	83
H5	2788	9951	2299	68
H8	2662	4068	319	69
H9	2470	3884	-965	86
H10	1091	5831	-1724	92
H11	-133	8003	-1215	95
H12	60	8239	60	81
H14	4698	4809	1081	70
H15	6317	2670	1619	85
H16	5369	1373	2611	87
H17	2771	2179	3063	81
H18	1111	4288	2501	64
H20	4069	6814	2915	77
H21	5408	4987	3772	103
H22	4115	3963	4744	112
H23	1454	4734	4873	110
H24	76	6557	4010	85
H26	-1373	10976	2435	82
H27	-2185	13144	2970	102
H28	-1142	13329	4045	107
H29	733	11391	4582	104
H30	1590	9210	4045	84

Table S18. Torsion angles [°] for neijk31.

C13-P1-C1-C2	87.52(19)	C10-C11-C12-C7	-0.2(4)
C7-P1-C1-C2	-23.9(2)	C8-C7-C12-C11	-0.7(4)
Fe1-P1-C1-C2	-150.06(17)	P1-C7-C12-C11	-176.9(2)
C13-P1-C1-C6	-91.85(16)	C7-P1-C13-C18	-116.57(18)
C7-P1-C1-C6	156.71(16)	C1-P1-C13-C18	133.92(18)
Fe1-P1-C1-C6	30.57(16)	Fe1-P1-C13-C18	22.3(2)
C6-C1-C2-C3	1.5(3)	C7-P1-C13-C14	64.5(2)
P1-C1-C2-C3	-177.86(19)	C1-P1-C13-C14	-45.0(2)
C1-C2-C3-C4	-1.4(4)	Fe1-P1-C13-C14	-156.64(16)
C2-C3-C4-C5	0.4(4)	C18-C13-C14-C15	1.2(4)
C3-C4-C5-C6	0.6(4)	P1-C13-C14-C15	-179.83(19)
C4-C5-C6-C1	-0.6(3)	C13-C14-C15-C16	-1.5(4)
C4-C5-C6-P2	179.68(19)	C14-C15-C16-C17	0.6(4)
C2-C1-C6-C5	-0.5(3)	C15-C16-C17-C18	0.6(4)
P1-C1-C6-C5	178.89(16)	C14-C13-C18-C17	-0.1(3)
C2-C1-C6-P2	179.26(16)	P1-C13-C18-C17	-179.06(18)
P1-C1-C6-P2	-1.3(2)	C16-C17-C18-C13	-0.8(4)
C19-P2-C6-C5	-88.77(19)	C25-P2-C19-C20	-97.5(2)
C25-P2-C6-C5	22.6(2)	C6-P2-C19-C20	13.0(2)
Fe1-P2-C6-C5	151.04(17)	Fe1-P2-C19-C20	124.98(19)
C19-P2-C6-C1	91.47(17)	C25-P2-C19-C24	84.6(2)
C25-P2-C6-C1	-157.14(16)	C6-P2-C19-C24	-164.79(19)
Fe1-P2-C6-C1	-28.72(16)	Fe1-P2-C19-C24	-52.9(2)
C13-P1-C7-C12	-175.25(18)	C24-C19-C20-C21	-0.1(4)
C1-P1-C7-C12	-66.0(2)	P2-C19-C20-C21	-178.0(2)
Fe1-P1-C7-C12	47.5(2)	C19-C20-C21-C22	-0.2(5)
C13-P1-C7-C8	8.7(2)	C20-C21-C22-C23	0.3(5)
C1-P1-C7-C8	117.94(19)	C21-C22-C23-C24	0.1(5)
Fe1-P1-C7-C8	-128.57(17)	C20-C19-C24-C23	0.5(4)
C12-C7-C8-C9	1.2(3)	P2-C19-C24-C23	178.4(2)
P1-C7-C8-C9	177.18(18)	C22-C23-C24-C19	-0.4(5)
C7-C8-C9-C10	-0.8(4)	C19-P2-C25-C26	-167.13(19)
C8-C9-C10-C11	-0.2(4)	C6-P2-C25-C26	81.8(2)
C9-C10-C11-C12	0.7(5)	Fe1-P2-C25-C26	-33.6(2)

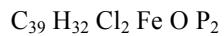
C19-P2-C25-C30	12.8(2)	C26-C27-C28-C29	0.5(5)
C6-P2-C25-C30	-98.3(2)	C27-C28-C29-C30	-0.1(5)
Fe1-P2-C25-C30	146.24(19)	C26-C25-C30-C29	-0.9(4)
C30-C25-C26-C27	1.3(4)	P2-C25-C30-C29	179.3(2)
P2-C25-C26-C27	-178.8(2)	C28-C29-C30-C25	0.2(5)
C25-C26-C27-C28	-1.1(5)		

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### 3.4 FeCl<sub>2</sub>(Xantphos)

REFERENCE NUMBER: neivf02

### CRYSTAL STRUCTURE REPORT



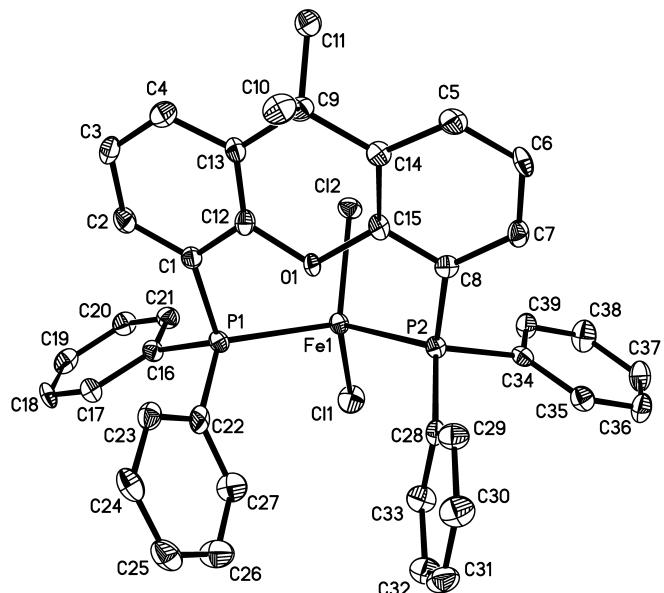
or



Report prepared for:

V. Fleischauer, Prof. M. Neidig

March 10, 2014



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#### Data collection

A crystal ( $0.26 \times 0.12 \times 0.06 \text{ mm}^3$ ) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at  $100.0(5) \text{ K}$ .<sup>1</sup> A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 5.03 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with  $0.50^\circ$  steps in  $\omega$  at six different  $\phi$  settings and a detector position of  $-33^\circ$  in  $2\theta$ . The intensity data were corrected for absorption.<sup>2</sup> Final cell constants were calculated from the xyz centroids of 4070 strong reflections from the actual data collection after integration.<sup>3</sup> See Table 1 for additional crystal and refinement information.

#### Structure solution and refinement

The structure was solved using SIR2011<sup>4</sup> and refined using SHELXL-2014.<sup>5</sup> The space group  $P2_1/n$  was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to  $R1 = 0.0581 (F^2, I > 2\sigma(I))$  and  $wR2 = 0.1388 (F^2, \text{all data})$ .

#### Structure description

The structure is the one suggested. The asymmetric unit contains two independent molecules in general positions.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

<sup>1</sup> APEX2, version 2013.10-0; Bruker AXS: Madison, WI, 2013.

<sup>2</sup> Sheldrick, G. M. SADABS, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.

<sup>3</sup> SAINT, version 8.34A; Bruker AXS: Madison, WI, 2013.

<sup>4</sup> Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. SIR2011: a new package for crystal structure determination and refinement, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.

<sup>5</sup> Sheldrick, G. M. SHELXL-2014/1; University of Göttingen: Göttingen, Germany, 2014.

Some equations of interest:

$$R_{\text{int}} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R1 = \sum ||F_o|| - |F_c|| / \sum |F_o|$$

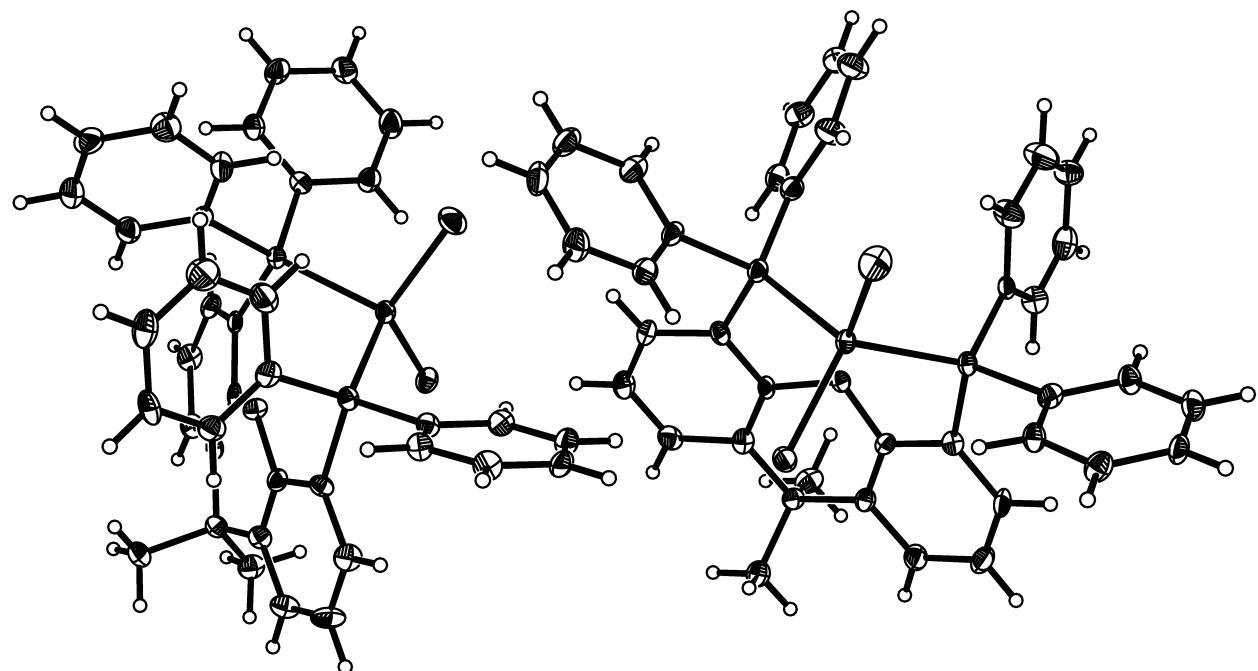
$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

where  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\sum [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where  $m$  = number of reflections and  $n$  = number of parameters



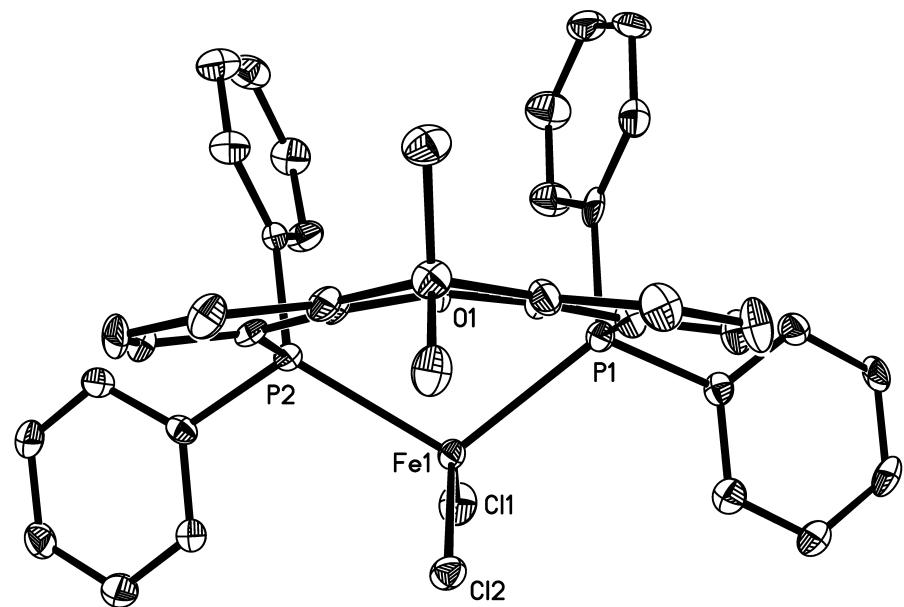
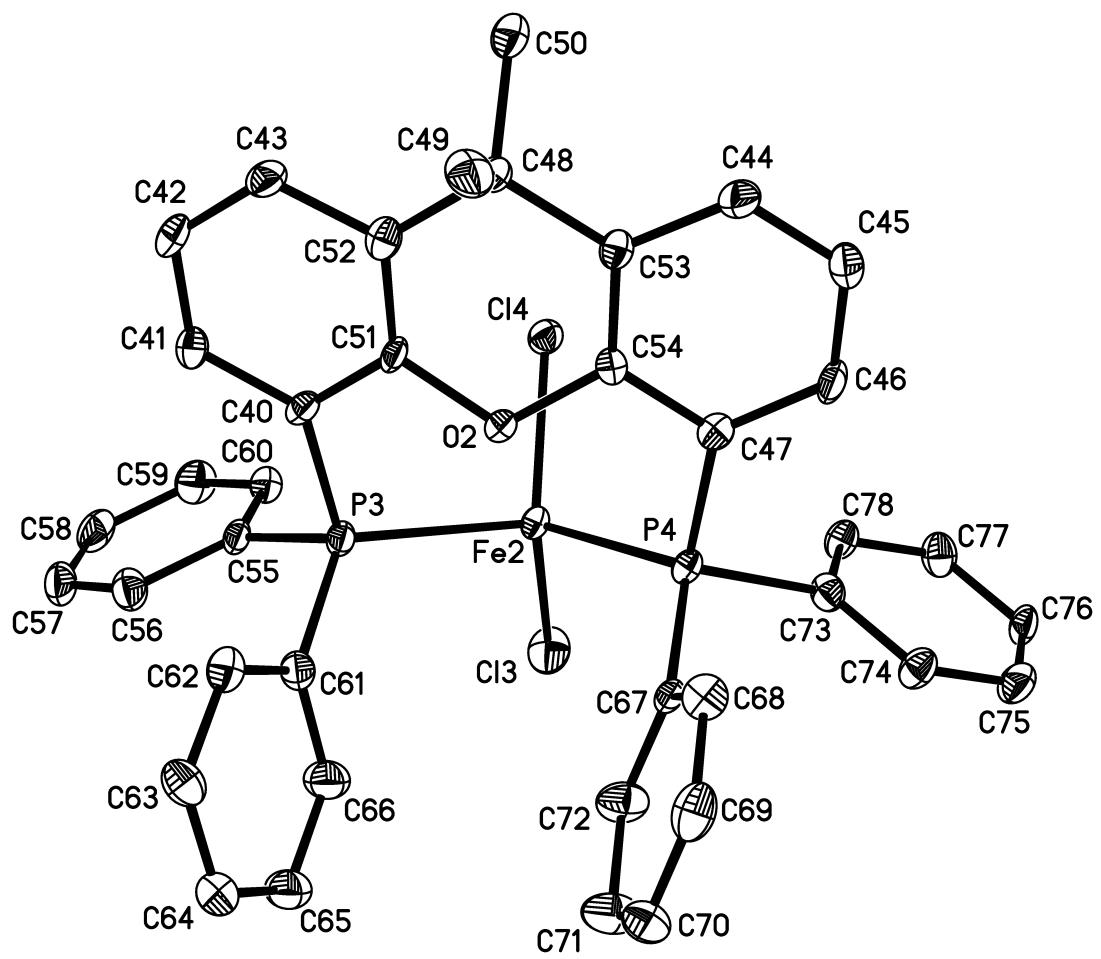


Table S19. Crystal data and structure refinement for neivf02.

Identification code	neivf02	
Empirical formula	C39 H32 Cl2 Fe O P2	
Formula weight	705.33	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	
Unit cell dimensions	<i>a</i> = 16.882(4) Å	α = 90°
	<i>b</i> = 10.534(3) Å	β = 93.412(4)°
	<i>c</i> = 37.753(9) Å	γ = 90°
Volume	6702(3) Å <sup>3</sup>	
<i>Z</i>	8	
Density (calculated)	1.398 Mg/m <sup>3</sup>	
Absorption coefficient	0.736 mm <sup>-1</sup>	
<i>F</i> (000)	2912	
Crystal color, morphology	colorless, plate	
Crystal size	0.26 x 0.12 x 0.06 mm <sup>3</sup>	
Theta range for data collection	1.963 to 27.519°	
Index ranges	-21 ≤ <i>h</i> ≤ 21, -13 ≤ <i>k</i> ≤ 13, -49 ≤ <i>l</i> ≤ 49	
Reflections collected	121316	
Independent reflections	15389 [ <i>R</i> (int) = 0.1290]	
Observed reflections	8852	
Completeness to theta = 27.485°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7456 and 0.6259	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameters	15389 / 0 / 815	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.027	
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> 1 = 0.0581, <i>wR</i> 2 = 0.1198	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1202, <i>wR</i> 2 = 0.1388	
Largest diff. peak and hole	0.901 and -0.467 e.Å <sup>-3</sup>	

Table S20. Atomic coordinates ( $x \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neivf02.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
Fe1	3336(1)	3368(1)	1194(1)	15(1)
Cl1	3986(1)	2666(1)	741(1)	27(1)
Cl2	3142(1)	2153(1)	1673(1)	19(1)
P1	3987(1)	5322(1)	1416(1)	15(1)
P2	1975(1)	3862(1)	970(1)	14(1)
O1	2407(1)	5200(2)	1616(1)	15(1)
C1	3685(2)	5610(4)	1862(1)	16(1)
C2	4200(2)	5867(4)	2156(1)	22(1)
C3	3910(3)	5984(4)	2490(1)	26(1)
C4	3108(3)	5820(4)	2536(1)	24(1)
C5	534(2)	4189(4)	1962(1)	21(1)
C6	174(2)	3634(4)	1659(1)	21(1)
C7	575(2)	3567(4)	1352(1)	18(1)
C8	1344(2)	4064(4)	1339(1)	14(1)
C9	1684(2)	5321(4)	2302(1)	18(1)
C10	1288(3)	6607(4)	2364(1)	24(1)
C11	1591(2)	4456(4)	2625(1)	23(1)
C12	2876(2)	5463(4)	1922(1)	16(1)
C13	2567(2)	5530(4)	2251(1)	17(1)
C14	1295(2)	4700(4)	1967(1)	16(1)
C15	1672(2)	4656(4)	1650(1)	14(1)
C16	5065(2)	5177(4)	1469(1)	16(1)
C17	5581(2)	6188(4)	1436(1)	19(1)
C18	6400(2)	5997(4)	1470(1)	20(1)
C19	6700(2)	4808(4)	1546(1)	22(1)
C20	6188(2)	3789(4)	1582(1)	22(1)
C21	5375(2)	3966(4)	1542(1)	20(1)
C22	3827(2)	6811(4)	1176(1)	19(1)
C23	3737(2)	7968(4)	1345(1)	21(1)
C24	3661(2)	9093(4)	1148(1)	23(1)
C25	3655(3)	9036(4)	782(1)	28(1)

C26	3737(3)	7891(4)	615(1)	32(1)
C27	3823(3)	6783(4)	809(1)	27(1)
C28	1782(2)	5198(4)	676(1)	16(1)
C29	1167(3)	6053(4)	713(1)	23(1)
C30	1027(3)	7005(4)	465(1)	28(1)
C31	1484(3)	7106(4)	176(1)	28(1)
C32	2095(3)	6254(4)	135(1)	27(1)
C33	2246(2)	5319(4)	385(1)	23(1)
C34	1542(2)	2558(4)	704(1)	16(1)
C35	950(2)	2741(4)	433(1)	20(1)
C36	697(2)	1736(4)	220(1)	24(1)
C37	1020(2)	548(4)	273(1)	25(1)
C38	1602(3)	339(4)	542(1)	28(1)
C39	1859(2)	1350(4)	757(1)	20(1)
Fe2	8354(1)	821(1)	1174(1)	14(1)
Cl3	8999(1)	1446(1)	708(1)	29(1)
Cl4	8165(1)	2042(1)	1653(1)	19(1)
P3	6981(1)	334(1)	969(1)	15(1)
P4	9000(1)	-1135(1)	1400(1)	14(1)
O2	7423(1)	-1032(2)	1608(1)	14(1)
C40	6357(2)	129(4)	1345(1)	15(1)
C41	5596(2)	642(4)	1358(1)	18(1)
C42	5202(2)	555(4)	1669(1)	22(1)
C43	5562(2)	7(4)	1970(1)	20(1)
C44	8148(2)	-1670(4)	2525(1)	24(1)
C45	8949(2)	-1833(4)	2472(1)	26(1)
C46	9229(2)	-1718(4)	2135(1)	20(1)
C47	8706(2)	-1438(4)	1851(1)	15(1)
C48	6718(2)	-1150(4)	2301(1)	16(1)
C49	6316(2)	-2437(4)	2366(1)	24(1)
C50	6645(2)	-285(4)	2628(1)	23(1)
C51	6686(2)	-473(4)	1651(1)	14(1)
C52	6324(2)	-531(4)	1970(1)	17(1)
C53	7600(2)	-1375(4)	2244(1)	16(1)
C54	7902(2)	-1281(4)	1913(1)	14(1)
C55	6528(2)	1651(4)	717(1)	19(1)

C56	5913(2)	1465(4)	456(1)	23(1)
C57	5586(2)	2508(5)	272(1)	28(1)
C58	5865(3)	3706(4)	344(1)	26(1)
C59	6473(3)	3905(4)	601(1)	27(1)
C60	6803(2)	2865(4)	784(1)	20(1)
C61	6782(2)	-1006(4)	677(1)	18(1)
C62	6164(2)	-1860(4)	720(1)	21(1)
C63	6004(2)	-2826(4)	476(1)	23(1)
C64	6461(2)	-2929(4)	186(1)	26(1)
C65	7073(3)	-2087(4)	134(1)	28(1)
C66	7235(3)	-1135(4)	381(1)	27(1)
C67	8840(2)	-2625(4)	1158(1)	14(1)
C68	8724(2)	-3786(4)	1323(1)	21(1)
C69	8646(2)	-4883(4)	1124(1)	26(1)
C70	8681(2)	-4842(4)	761(1)	26(1)
C71	8791(3)	-3701(5)	592(1)	34(1)
C72	8863(3)	-2583(4)	789(1)	26(1)
C73	10076(2)	-985(4)	1456(1)	18(1)
C74	10598(2)	-2012(4)	1424(1)	20(1)
C75	11408(2)	-1802(4)	1462(1)	23(1)
C76	11704(2)	-592(4)	1531(1)	21(1)
C77	11202(2)	415(4)	1564(1)	23(1)
C78	10385(2)	224(4)	1518(1)	18(1)

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Table S21. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for neivf02.

Fe(1)-Cl(1)	2.2137(12)	C(10)-H(10C)	0.9800
Fe(1)-Cl(2)	2.2548(12)	C(11)-H(11A)	0.9800
Fe(1)-P(1)	2.4564(13)	C(11)-H(11B)	0.9800
Fe(1)-P(2)	2.4572(13)	C(11)-H(11C)	0.9800
P(1)-C(1)	1.814(4)	C(12)-C(13)	1.377(5)
P(1)-C(22)	1.823(4)	C(14)-C(15)	1.389(5)
P(1)-C(16)	1.825(4)	C(16)-C(17)	1.385(5)
P(2)-C(28)	1.811(4)	C(16)-C(21)	1.400(5)
P(2)-C(8)	1.817(4)	C(17)-C(18)	1.396(5)
P(2)-C(34)	1.827(4)	C(17)-H(17)	0.9500
O(1)-C(15)	1.381(4)	C(18)-C(19)	1.375(6)
O(1)-C(12)	1.391(4)	C(18)-H(18)	0.9500
C(1)-C(2)	1.395(5)	C(19)-C(20)	1.390(6)
C(1)-C(12)	1.406(5)	C(19)-H(19)	0.9500
C(2)-C(3)	1.384(5)	C(20)-C(21)	1.384(5)
C(2)-H(2)	0.9500	C(20)-H(20)	0.9500
C(3)-C(4)	1.386(6)	C(21)-H(21)	0.9500
C(3)-H(3)	0.9500	C(22)-C(27)	1.386(6)
C(4)-C(13)	1.404(5)	C(22)-C(23)	1.387(6)
C(4)-H(4)	0.9500	C(23)-C(24)	1.401(6)
C(5)-C(6)	1.391(6)	C(23)-H(23)	0.9500
C(5)-C(14)	1.392(5)	C(24)-C(25)	1.384(6)
C(5)-H(5)	0.9500	C(24)-H(24)	0.9500
C(6)-C(7)	1.381(5)	C(25)-C(26)	1.372(6)
C(6)-H(6)	0.9500	C(25)-H(25)	0.9500
C(7)-C(8)	1.403(5)	C(26)-C(27)	1.382(6)
C(7)-H(7)	0.9500	C(26)-H(26)	0.9500
C(8)-C(15)	1.413(5)	C(27)-H(27)	0.9500
C(9)-C(13)	1.530(5)	C(28)-C(29)	1.388(5)
C(9)-C(10)	1.535(5)	C(28)-C(33)	1.392(5)
C(9)-C(11)	1.536(5)	C(29)-C(30)	1.382(6)
C(9)-C(14)	1.536(5)	C(29)-H(29)	0.9500
C(10)-H(10A)	0.9800	C(30)-C(31)	1.379(6)
C(10)-H(10B)	0.9800	C(30)-H(30)	0.9500

C(31)-C(32)	1.383(6)	C(44)-C(45)	1.391(6)
C(31)-H(31)	0.9500	C(44)-C(53)	1.401(5)
C(32)-C(33)	1.378(6)	C(44)-H(44)	0.9500
C(32)-H(32)	0.9500	C(45)-C(46)	1.392(5)
C(33)-H(33)	0.9500	C(45)-H(45)	0.9500
C(34)-C(39)	1.390(5)	C(46)-C(47)	1.379(5)
C(34)-C(35)	1.401(5)	C(46)-H(46)	0.9500
C(35)-C(36)	1.383(6)	C(47)-C(54)	1.401(5)
C(35)-H(35)	0.9500	C(48)-C(52)	1.529(5)
C(36)-C(37)	1.376(6)	C(48)-C(53)	1.536(5)
C(36)-H(36)	0.9500	C(48)-C(49)	1.542(5)
C(37)-C(38)	1.388(6)	C(48)-C(50)	1.543(5)
C(37)-H(37)	0.9500	C(49)-H(49A)	0.9800
C(38)-C(39)	1.392(6)	C(49)-H(49B)	0.9800
C(38)-H(38)	0.9500	C(49)-H(49C)	0.9800
C(39)-H(39)	0.9500	C(50)-H(50A)	0.9800
Fe(2)-Cl(3)	2.2247(12)	C(50)-H(50B)	0.9800
Fe(2)-Cl(4)	2.2565(12)	C(50)-H(50C)	0.9800
Fe(2)-P(3)	2.4543(13)	C(51)-C(52)	1.383(5)
Fe(2)-P(4)	2.4595(13)	C(53)-C(54)	1.382(5)
P(3)-C(61)	1.811(4)	C(55)-C(60)	1.380(6)
P(3)-C(55)	1.824(4)	C(55)-C(56)	1.401(5)
P(3)-C(40)	1.831(4)	C(56)-C(57)	1.396(6)
P(4)-C(73)	1.822(4)	C(56)-H(56)	0.9500
P(4)-C(67)	1.827(4)	C(57)-C(58)	1.368(6)
P(4)-C(47)	1.831(4)	C(57)-H(57)	0.9500
O(2)-C(54)	1.390(4)	C(58)-C(59)	1.384(6)
O(2)-C(51)	1.395(4)	C(58)-H(58)	0.9500
C(40)-C(41)	1.397(5)	C(59)-C(60)	1.395(6)
C(40)-C(51)	1.401(5)	C(59)-H(59)	0.9500
C(41)-C(42)	1.388(5)	C(60)-H(60)	0.9500
C(41)-H(41)	0.9500	C(61)-C(62)	1.395(5)
C(42)-C(43)	1.380(6)	C(61)-C(66)	1.398(5)
C(42)-H(42)	0.9500	C(62)-C(63)	1.389(6)
C(43)-C(52)	1.406(5)	C(62)-H(62)	0.9500
C(43)-H(43)	0.9500	C(63)-C(64)	1.383(6)

C(63)-H(63)	0.9500	C(22)-P(1)-C(16)	104.12(18)
C(64)-C(65)	1.384(6)	C(1)-P(1)-Fe(1)	108.13(13)
C(64)-H(64)	0.9500	C(22)-P(1)-Fe(1)	120.12(14)
C(65)-C(66)	1.385(6)	C(16)-P(1)-Fe(1)	112.97(13)
C(65)-H(65)	0.9500	C(28)-P(2)-C(8)	106.72(18)
C(66)-H(66)	0.9500	C(28)-P(2)-C(34)	101.32(18)
C(67)-C(68)	1.390(5)	C(8)-P(2)-C(34)	106.02(18)
C(67)-C(72)	1.397(5)	C(28)-P(2)-Fe(1)	120.42(13)
C(68)-C(69)	1.381(6)	C(8)-P(2)-Fe(1)	109.82(13)
C(68)-H(68)	0.9500	C(34)-P(2)-Fe(1)	111.42(13)
C(69)-C(70)	1.374(6)	C(15)-O(1)-C(12)	118.3(3)
C(69)-H(69)	0.9500	C(2)-C(1)-C(12)	117.2(4)
C(70)-C(71)	1.378(6)	C(2)-C(1)-P(1)	125.0(3)
C(70)-H(70)	0.9500	C(12)-C(1)-P(1)	117.5(3)
C(71)-C(72)	1.394(6)	C(3)-C(2)-C(1)	120.3(4)
C(71)-H(71)	0.9500	C(3)-C(2)-H(2)	119.9
C(72)-H(72)	0.9500	C(1)-C(2)-H(2)	119.9
C(73)-C(78)	1.392(5)	C(2)-C(3)-C(4)	120.4(4)
C(73)-C(74)	1.405(5)	C(2)-C(3)-H(3)	119.8
C(74)-C(75)	1.385(5)	C(4)-C(3)-H(3)	119.8
C(74)-H(74)	0.9500	C(3)-C(4)-C(13)	121.7(4)
C(75)-C(76)	1.388(6)	C(3)-C(4)-H(4)	119.2
C(75)-H(75)	0.9500	C(13)-C(4)-H(4)	119.2
C(76)-C(77)	1.369(5)	C(6)-C(5)-C(14)	122.1(4)
C(76)-H(76)	0.9500	C(6)-C(5)-H(5)	118.9
C(77)-C(78)	1.393(5)	C(14)-C(5)-H(5)	118.9
C(77)-H(77)	0.9500	C(7)-C(6)-C(5)	120.0(4)
C(78)-H(78)	0.9500	C(7)-C(6)-H(6)	120.0
Cl(1)-Fe(1)-Cl(2)	122.12(5)	C(5)-C(6)-H(6)	120.0
Cl(1)-Fe(1)-P(1)	108.13(4)	C(6)-C(7)-C(8)	120.7(4)
Cl(2)-Fe(1)-P(1)	106.62(4)	C(6)-C(7)-H(7)	119.6
Cl(1)-Fe(1)-P(2)	107.50(5)	C(8)-C(7)-H(7)	119.6
Cl(2)-Fe(1)-P(2)	102.66(4)	C(7)-C(8)-C(15)	117.0(3)
P(1)-Fe(1)-P(2)	109.30(4)	C(7)-C(8)-P(2)	124.6(3)
C(1)-P(1)-C(22)	105.96(19)	C(15)-C(8)-P(2)	118.1(3)
C(1)-P(1)-C(16)	104.26(18)	C(13)-C(9)-C(10)	109.2(3)

C(13)-C(9)-C(11)	109.4(3)	C(19)-C(18)-H(18)	120.0
C(10)-C(9)-C(11)	109.7(3)	C(17)-C(18)-H(18)	120.0
C(13)-C(9)-C(14)	109.2(3)	C(18)-C(19)-C(20)	120.0(4)
C(10)-C(9)-C(14)	109.4(3)	C(18)-C(19)-H(19)	120.0
C(11)-C(9)-C(14)	109.9(3)	C(20)-C(19)-H(19)	120.0
C(9)-C(10)-H(10A)	109.5	C(21)-C(20)-C(19)	120.2(4)
C(9)-C(10)-H(10B)	109.5	C(21)-C(20)-H(20)	119.9
H(10A)-C(10)-H(10B)	109.5	C(19)-C(20)-H(20)	119.9
C(9)-C(10)-H(10C)	109.5	C(20)-C(21)-C(16)	120.1(4)
H(10A)-C(10)-H(10C)	109.5	C(20)-C(21)-H(21)	120.0
H(10B)-C(10)-H(10C)	109.5	C(16)-C(21)-H(21)	120.0
C(9)-C(11)-H(11A)	109.5	C(27)-C(22)-C(23)	118.9(4)
C(9)-C(11)-H(11B)	109.5	C(27)-C(22)-P(1)	118.0(3)
H(11A)-C(11)-H(11B)	109.5	C(23)-C(22)-P(1)	123.1(3)
C(9)-C(11)-H(11C)	109.5	C(22)-C(23)-C(24)	120.6(4)
H(11A)-C(11)-H(11C)	109.5	C(22)-C(23)-H(23)	119.7
H(11B)-C(11)-H(11C)	109.5	C(24)-C(23)-H(23)	119.7
C(13)-C(12)-O(1)	122.2(3)	C(25)-C(24)-C(23)	119.2(4)
C(13)-C(12)-C(1)	124.4(4)	C(25)-C(24)-H(24)	120.4
O(1)-C(12)-C(1)	113.4(3)	C(23)-C(24)-H(24)	120.4
C(12)-C(13)-C(4)	116.0(4)	C(26)-C(25)-C(24)	120.2(4)
C(12)-C(13)-C(9)	122.0(3)	C(26)-C(25)-H(25)	119.9
C(4)-C(13)-C(9)	121.9(4)	C(24)-C(25)-H(25)	119.9
C(15)-C(14)-C(5)	116.4(4)	C(25)-C(26)-C(27)	120.6(5)
C(15)-C(14)-C(9)	121.9(3)	C(25)-C(26)-H(26)	119.7
C(5)-C(14)-C(9)	121.7(3)	C(27)-C(26)-H(26)	119.7
O(1)-C(15)-C(14)	121.9(3)	C(26)-C(27)-C(22)	120.5(4)
O(1)-C(15)-C(8)	114.5(3)	C(26)-C(27)-H(27)	119.8
C(14)-C(15)-C(8)	123.7(3)	C(22)-C(27)-H(27)	119.8
C(17)-C(16)-C(21)	119.3(4)	C(29)-C(28)-C(33)	118.8(4)
C(17)-C(16)-P(1)	123.6(3)	C(29)-C(28)-P(2)	123.3(3)
C(21)-C(16)-P(1)	117.2(3)	C(33)-C(28)-P(2)	117.7(3)
C(16)-C(17)-C(18)	120.3(4)	C(30)-C(29)-C(28)	120.0(4)
C(16)-C(17)-H(17)	119.8	C(30)-C(29)-H(29)	120.0
C(18)-C(17)-H(17)	119.8	C(28)-C(29)-H(29)	120.0
C(19)-C(18)-C(17)	120.1(4)	C(31)-C(30)-C(29)	120.8(4)

C(31)-C(30)-H(30)	119.6	C(61)-P(3)-C(40)	106.63(18)
C(29)-C(30)-H(30)	119.6	C(55)-P(3)-C(40)	104.58(18)
C(30)-C(31)-C(32)	119.7(4)	C(61)-P(3)-Fe(2)	119.50(13)
C(30)-C(31)-H(31)	120.2	C(55)-P(3)-Fe(2)	111.40(14)
C(32)-C(31)-H(31)	120.2	C(40)-P(3)-Fe(2)	110.86(13)
C(33)-C(32)-C(31)	119.7(4)	C(73)-P(4)-C(67)	104.47(18)
C(33)-C(32)-H(32)	120.1	C(73)-P(4)-C(47)	103.33(18)
C(31)-C(32)-H(32)	120.1	C(67)-P(4)-C(47)	105.86(18)
C(32)-C(33)-C(28)	121.0(4)	C(73)-P(4)-Fe(2)	112.72(14)
C(32)-C(33)-H(33)	119.5	C(67)-P(4)-Fe(2)	119.85(13)
C(28)-C(33)-H(33)	119.5	C(47)-P(4)-Fe(2)	109.19(13)
C(39)-C(34)-C(35)	118.8(4)	C(54)-O(2)-C(51)	117.7(3)
C(39)-C(34)-P(2)	118.2(3)	C(41)-C(40)-C(51)	117.9(3)
C(35)-C(34)-P(2)	122.8(3)	C(41)-C(40)-P(3)	123.6(3)
C(36)-C(35)-C(34)	120.2(4)	C(51)-C(40)-P(3)	118.3(3)
C(36)-C(35)-H(35)	119.9	C(42)-C(41)-C(40)	119.4(4)
C(34)-C(35)-H(35)	119.9	C(42)-C(41)-H(41)	120.3
C(37)-C(36)-C(35)	120.3(4)	C(40)-C(41)-H(41)	120.3
C(37)-C(36)-H(36)	119.8	C(43)-C(42)-C(41)	120.9(4)
C(35)-C(36)-H(36)	119.8	C(43)-C(42)-H(42)	119.5
C(36)-C(37)-C(38)	120.6(4)	C(41)-C(42)-H(42)	119.5
C(36)-C(37)-H(37)	119.7	C(42)-C(43)-C(52)	121.8(4)
C(38)-C(37)-H(37)	119.7	C(42)-C(43)-H(43)	119.1
C(37)-C(38)-C(39)	119.2(4)	C(52)-C(43)-H(43)	119.1
C(37)-C(38)-H(38)	120.4	C(45)-C(44)-C(53)	121.5(4)
C(39)-C(38)-H(38)	120.4	C(45)-C(44)-H(44)	119.3
C(34)-C(39)-C(38)	120.9(4)	C(53)-C(44)-H(44)	119.3
C(34)-C(39)-H(39)	119.6	C(44)-C(45)-C(46)	120.5(4)
C(38)-C(39)-H(39)	119.6	C(44)-C(45)-H(45)	119.8
Cl(3)-Fe(2)-Cl(4)	124.40(5)	C(46)-C(45)-H(45)	119.8
Cl(3)-Fe(2)-P(3)	108.03(5)	C(47)-C(46)-C(45)	119.6(4)
Cl(4)-Fe(2)-P(3)	101.29(4)	C(47)-C(46)-H(46)	120.2
Cl(3)-Fe(2)-P(4)	107.09(4)	C(45)-C(46)-H(46)	120.2
Cl(4)-Fe(2)-P(4)	106.34(4)	C(46)-C(47)-C(54)	118.6(4)
P(3)-Fe(2)-P(4)	109.00(4)	C(46)-C(47)-P(4)	124.3(3)
C(61)-P(3)-C(55)	102.60(19)	C(54)-C(47)-P(4)	117.0(3)

C(52)-C(48)-C(53)	109.2(3)	C(58)-C(57)-C(56)	120.4(4)
C(52)-C(48)-C(49)	109.4(3)	C(58)-C(57)-H(57)	119.8
C(53)-C(48)-C(49)	109.1(3)	C(56)-C(57)-H(57)	119.8
C(52)-C(48)-C(50)	110.5(3)	C(57)-C(58)-C(59)	120.7(4)
C(53)-C(48)-C(50)	109.1(3)	C(57)-C(58)-H(58)	119.6
C(49)-C(48)-C(50)	109.6(3)	C(59)-C(58)-H(58)	119.6
C(48)-C(49)-H(49A)	109.5	C(58)-C(59)-C(60)	119.1(4)
C(48)-C(49)-H(49B)	109.5	C(58)-C(59)-H(59)	120.5
H(49A)-C(49)-H(49B)	109.5	C(60)-C(59)-H(59)	120.5
C(48)-C(49)-H(49C)	109.5	C(55)-C(60)-C(59)	121.1(4)
H(49A)-C(49)-H(49C)	109.5	C(55)-C(60)-H(60)	119.5
H(49B)-C(49)-H(49C)	109.5	C(59)-C(60)-H(60)	119.5
C(48)-C(50)-H(50A)	109.5	C(62)-C(61)-C(66)	118.7(4)
C(48)-C(50)-H(50B)	109.5	C(62)-C(61)-P(3)	123.0(3)
H(50A)-C(50)-H(50B)	109.5	C(66)-C(61)-P(3)	118.2(3)
C(48)-C(50)-H(50C)	109.5	C(63)-C(62)-C(61)	120.8(4)
H(50A)-C(50)-H(50C)	109.5	C(63)-C(62)-H(62)	119.6
H(50B)-C(50)-H(50C)	109.5	C(61)-C(62)-H(62)	119.6
C(52)-C(51)-O(2)	121.6(3)	C(64)-C(63)-C(62)	119.3(4)
C(52)-C(51)-C(40)	124.2(3)	C(64)-C(63)-H(63)	120.4
O(2)-C(51)-C(40)	114.2(3)	C(62)-C(63)-H(63)	120.4
C(51)-C(52)-C(43)	115.7(4)	C(63)-C(64)-C(65)	121.1(4)
C(51)-C(52)-C(48)	122.6(3)	C(63)-C(64)-H(64)	119.4
C(43)-C(52)-C(48)	121.7(4)	C(65)-C(64)-H(64)	119.4
C(54)-C(53)-C(44)	116.1(3)	C(64)-C(65)-C(66)	119.3(4)
C(54)-C(53)-C(48)	122.0(3)	C(64)-C(65)-H(65)	120.3
C(44)-C(53)-C(48)	121.9(3)	C(66)-C(65)-H(65)	120.3
C(53)-C(54)-O(2)	122.3(3)	C(65)-C(66)-C(61)	120.8(4)
C(53)-C(54)-C(47)	123.7(4)	C(65)-C(66)-H(66)	119.6
O(2)-C(54)-C(47)	114.0(3)	C(61)-C(66)-H(66)	119.6
C(60)-C(55)-C(56)	119.1(4)	C(68)-C(67)-C(72)	119.2(4)
C(60)-C(55)-P(3)	118.8(3)	C(68)-C(67)-P(4)	123.6(3)
C(56)-C(55)-P(3)	122.1(3)	C(72)-C(67)-P(4)	117.2(3)
C(57)-C(56)-C(55)	119.6(4)	C(69)-C(68)-C(67)	120.2(4)
C(57)-C(56)-H(56)	120.2	C(69)-C(68)-H(68)	119.9
C(55)-C(56)-H(56)	120.2	C(67)-C(68)-H(68)	119.9

C(70)-C(69)-C(68)	120.5(4)	C(75)-C(74)-C(73)	119.3(4)
C(70)-C(69)-H(69)	119.7	C(75)-C(74)-H(74)	120.4
C(68)-C(69)-H(69)	119.7	C(73)-C(74)-H(74)	120.4
C(69)-C(70)-C(71)	120.2(4)	C(74)-C(75)-C(76)	120.6(4)
C(69)-C(70)-H(70)	119.9	C(74)-C(75)-H(75)	119.7
C(71)-C(70)-H(70)	119.9	C(76)-C(75)-H(75)	119.7
C(70)-C(71)-C(72)	120.1(4)	C(77)-C(76)-C(75)	120.7(4)
C(70)-C(71)-H(71)	120.0	C(77)-C(76)-H(76)	119.7
C(72)-C(71)-H(71)	120.0	C(75)-C(76)-H(76)	119.7
C(71)-C(72)-C(67)	119.8(4)	C(76)-C(77)-C(78)	119.4(4)
C(71)-C(72)-H(72)	120.1	C(76)-C(77)-H(77)	120.3
C(67)-C(72)-H(72)	120.1	C(78)-C(77)-H(77)	120.3
C(78)-C(73)-C(74)	119.2(4)	C(73)-C(78)-C(77)	120.8(4)
C(78)-C(73)-P(4)	117.4(3)	C(73)-C(78)-H(78)	119.6
C(74)-C(73)-P(4)	123.3(3)	C(77)-C(78)-H(78)	119.6

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Table S22. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neivf02. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12} ]$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Fe1	11(1)	16(1)	17(1)	0(1)	1(1)	0(1)
Cl1	22(1)	35(1)	26(1)	-8(1)	7(1)	3(1)
Cl2	18(1)	20(1)	21(1)	5(1)	2(1)	1(1)
P1	11(1)	16(1)	18(1)	0(1)	3(1)	0(1)
P2	12(1)	13(1)	17(1)	0(1)	1(1)	1(1)
O1	9(1)	20(2)	16(1)	-1(1)	0(1)	-5(1)
C1	15(2)	17(2)	15(2)	-3(2)	4(2)	-2(2)
C2	14(2)	27(2)	24(2)	-2(2)	3(2)	-5(2)
C3	24(2)	34(3)	19(2)	-8(2)	-1(2)	-11(2)
C4	27(2)	27(2)	19(2)	-4(2)	4(2)	-3(2)
C5	14(2)	29(2)	21(2)	0(2)	6(2)	3(2)
C6	9(2)	25(2)	29(2)	-1(2)	2(2)	-5(2)
C7	12(2)	19(2)	23(2)	2(2)	-3(2)	1(2)
C8	12(2)	15(2)	17(2)	2(2)	1(2)	6(2)
C9	18(2)	20(2)	17(2)	-2(2)	3(2)	2(2)
C10	26(2)	23(2)	22(2)	-4(2)	4(2)	7(2)
C11	18(2)	30(3)	22(2)	-1(2)	2(2)	-2(2)
C12	12(2)	16(2)	20(2)	-1(2)	-2(2)	1(2)
C13	15(2)	15(2)	20(2)	-2(2)	1(2)	-3(2)
C14	11(2)	19(2)	18(2)	-1(2)	3(2)	4(2)
C15	5(2)	15(2)	22(2)	1(2)	0(2)	4(2)
C16	12(2)	19(2)	17(2)	-1(2)	4(2)	-1(2)
C17	18(2)	17(2)	23(2)	0(2)	2(2)	-2(2)
C18	13(2)	19(2)	28(2)	-1(2)	3(2)	-8(2)
C19	12(2)	34(3)	21(2)	-2(2)	-2(2)	6(2)
C20	17(2)	25(2)	23(2)	1(2)	0(2)	4(2)
C21	19(2)	23(2)	20(2)	1(2)	2(2)	-1(2)
C22	6(2)	29(2)	23(2)	-3(2)	-1(2)	-1(2)
C23	17(2)	25(2)	21(2)	-3(2)	0(2)	-1(2)
C24	22(2)	11(2)	37(3)	-2(2)	5(2)	2(2)
C25	24(2)	18(2)	41(3)	8(2)	1(2)	1(2)

C26	41(3)	29(3)	27(3)	4(2)	4(2)	2(2)
C27	32(3)	23(2)	27(3)	-3(2)	3(2)	4(2)
C28	14(2)	13(2)	20(2)	-2(2)	-4(2)	-1(2)
C29	27(2)	20(2)	22(2)	1(2)	3(2)	3(2)
C30	33(3)	22(2)	29(3)	2(2)	1(2)	7(2)
C31	42(3)	20(2)	21(2)	4(2)	-4(2)	0(2)
C32	29(2)	27(3)	25(2)	2(2)	6(2)	0(2)
C33	20(2)	22(2)	27(2)	3(2)	3(2)	6(2)
C34	17(2)	13(2)	17(2)	0(2)	4(2)	-2(2)
C35	19(2)	16(2)	24(2)	1(2)	2(2)	1(2)
C36	18(2)	27(2)	27(2)	-2(2)	-7(2)	-1(2)
C37	22(2)	20(2)	31(3)	-8(2)	-2(2)	-3(2)
C38	27(2)	19(2)	38(3)	-5(2)	-4(2)	3(2)
C39	18(2)	18(2)	24(2)	0(2)	-3(2)	-1(2)
Fe2	10(1)	15(1)	17(1)	1(1)	2(1)	1(1)
Cl3	23(1)	39(1)	26(1)	11(1)	8(1)	-2(1)
Cl4	17(1)	18(1)	21(1)	-4(1)	1(1)	1(1)
P3	10(1)	19(1)	16(1)	1(1)	1(1)	1(1)
P4	10(1)	15(1)	18(1)	0(1)	2(1)	1(1)
O2	12(1)	18(2)	14(1)	-1(1)	2(1)	2(1)
C40	11(2)	16(2)	19(2)	-2(2)	4(2)	1(2)
C41	15(2)	18(2)	21(2)	3(2)	-2(2)	4(2)
C42	10(2)	28(2)	27(2)	0(2)	4(2)	2(2)
C43	15(2)	26(2)	20(2)	-3(2)	6(2)	-2(2)
C44	22(2)	34(3)	17(2)	3(2)	5(2)	9(2)
C45	19(2)	40(3)	20(2)	3(2)	-2(2)	8(2)
C46	11(2)	24(2)	23(2)	4(2)	2(2)	7(2)
C47	15(2)	14(2)	17(2)	2(2)	3(2)	-1(2)
C48	11(2)	22(2)	15(2)	-1(2)	3(2)	-2(2)
C49	23(2)	30(3)	18(2)	6(2)	2(2)	-4(2)
C50	13(2)	30(3)	26(2)	-3(2)	1(2)	0(2)
C51	6(2)	16(2)	20(2)	-3(2)	1(2)	1(2)
C52	13(2)	15(2)	23(2)	1(2)	1(2)	-3(2)
C53	12(2)	17(2)	18(2)	1(2)	1(2)	-1(2)
C54	13(2)	15(2)	15(2)	1(2)	-1(2)	0(2)
C55	11(2)	33(3)	14(2)	3(2)	2(2)	5(2)

C56	19(2)	30(3)	20(2)	4(2)	-1(2)	0(2)
C57	18(2)	42(3)	22(2)	4(2)	-3(2)	6(2)
C58	23(2)	26(3)	30(3)	7(2)	3(2)	12(2)
C59	30(2)	19(2)	32(3)	3(2)	1(2)	5(2)
C60	16(2)	23(2)	22(2)	-2(2)	0(2)	0(2)
C61	16(2)	21(2)	18(2)	1(2)	-1(2)	1(2)
C62	17(2)	22(2)	24(2)	3(2)	1(2)	0(2)
C63	24(2)	21(2)	24(2)	-2(2)	-3(2)	-6(2)
C64	23(2)	28(3)	25(2)	-6(2)	-2(2)	1(2)
C65	25(2)	35(3)	24(2)	-8(2)	5(2)	-2(2)
C66	24(2)	34(3)	24(2)	-8(2)	5(2)	-5(2)
C67	10(2)	13(2)	19(2)	-3(2)	1(2)	2(2)
C68	21(2)	17(2)	24(2)	2(2)	3(2)	-3(2)
C69	18(2)	23(2)	37(3)	6(2)	3(2)	-1(2)
C70	27(2)	26(3)	25(2)	-9(2)	-3(2)	-2(2)
C71	46(3)	31(3)	24(3)	-6(2)	6(2)	2(2)
C72	38(3)	15(2)	25(2)	-1(2)	4(2)	2(2)
C73	13(2)	23(2)	17(2)	2(2)	1(2)	-3(2)
C74	14(2)	20(2)	27(2)	-2(2)	4(2)	-1(2)
C75	15(2)	28(3)	28(3)	-3(2)	4(2)	3(2)
C76	10(2)	29(2)	23(2)	1(2)	1(2)	4(2)
C77	19(2)	20(2)	28(2)	2(2)	-3(2)	-3(2)
C78	17(2)	13(2)	24(2)	2(2)	2(2)	2(2)

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Table S23. Hydrogen coordinates ( $x \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neivf02.

	x	y	z	U(eq)
H2	4752	5961	2127	26
H3	4263	6178	2688	31
H4	2920	5906	2767	29
H5	251	4221	2172	25
H6	-348	3300	1664	25
H7	328	3181	1146	22
H10A	1335	7148	2155	36
H10B	1550	7020	2572	36
H10C	726	6475	2405	36
H11A	1878	3660	2592	35
H11B	1028	4274	2648	35
H11C	1809	4883	2840	35
H17	5375	7015	1389	23
H18	6751	6688	1439	24
H19	7258	4684	1576	27
H20	6397	2967	1633	26
H21	5027	3266	1565	24
H23	3726	7997	1596	25
H24	3614	9886	1265	28
H25	3595	9792	645	33
H26	3733	7859	363	39
H27	3881	5996	690	32
H29	842	5984	910	27
H30	612	7597	495	34
H31	1379	7757	5	34
H32	2409	6314	-65	32
H33	2674	4747	358	28
H35	722	3558	396	24
H36	297	1867	35	29
H37	843	-136	124	30

H38	1821	-484	579	34
H39	2256	1212	942	24
H41	5350	1047	1155	22
H42	4678	878	1676	26
H43	5287	-8	2182	24
H44	7967	-1761	2758	29
H45	9309	-2024	2669	32
H46	9777	-1832	2100	23
H49A	6360	-2984	2158	36
H49B	5754	-2299	2407	36
H49C	6577	-2846	2575	36
H50A	6887	-706	2839	34
H50B	6084	-118	2661	34
H50C	6920	519	2590	34
H56	5720	634	404	28
H57	5168	2385	96	33
H58	5638	4408	217	32
H59	6663	4739	651	32
H60	7224	2995	959	24
H62	5849	-1781	920	25
H63	5585	-3408	508	28
H64	6353	-3589	18	31
H65	7379	-2162	-68	34
H66	7660	-563	349	33
H68	8698	-3824	1573	25
H69	8567	-5672	1238	31
H70	8629	-5603	626	31
H71	8817	-3677	342	40
H72	8929	-1794	673	31
H74	10397	-2842	1378	24
H75	11764	-2491	1440	28
H76	12262	-462	1556	25
H77	11407	1237	1618	27
H78	10036	928	1529	22

Table S24. Torsion angles [°] for neivf02.

C22-P1-C1-C2	-100.1(4)	C14-C9-C13-C12	15.2(5)
C16-P1-C1-C2	9.5(4)	C10-C9-C13-C4	74.6(5)
Fe1-P1-C1-C2	129.9(3)	C11-C9-C13-C4	-45.5(5)
C22-P1-C1-C12	85.4(3)	C14-C9-C13-C4	-165.8(4)
C16-P1-C1-C12	-165.1(3)	C6-C5-C14-C15	1.6(6)
Fe1-P1-C1-C12	-44.6(3)	C6-C5-C14-C9	179.5(4)
C12-C1-C2-C3	-0.9(6)	C13-C9-C14-C15	-14.2(5)
P1-C1-C2-C3	-175.4(3)	C10-C9-C14-C15	105.3(4)
C1-C2-C3-C4	1.4(7)	C11-C9-C14-C15	-134.2(4)
C2-C3-C4-C13	0.1(7)	C13-C9-C14-C5	168.1(4)
C14-C5-C6-C7	0.5(6)	C10-C9-C14-C5	-72.4(5)
C5-C6-C7-C8	-0.5(6)	C11-C9-C14-C5	48.1(5)
C6-C7-C8-C15	-1.6(6)	C12-O1-C15-C14	19.0(5)
C6-C7-C8-P2	172.1(3)	C12-O1-C15-C8	-161.2(3)
C28-P2-C8-C7	91.0(4)	C5-C14-C15-O1	175.9(3)
C34-P2-C8-C7	-16.4(4)	C9-C14-C15-O1	-2.0(6)
Fe1-P2-C8-C7	-136.9(3)	C5-C14-C15-C8	-3.9(6)
C28-P2-C8-C15	-95.4(3)	C9-C14-C15-C8	178.2(4)
C34-P2-C8-C15	157.2(3)	C7-C8-C15-O1	-175.9(3)
Fe1-P2-C8-C15	36.7(3)	P2-C8-C15-O1	10.0(4)
C15-O1-C12-C13	-18.1(5)	C7-C8-C15-C14	3.9(6)
C15-O1-C12-C1	160.1(3)	P2-C8-C15-C14	-170.2(3)
C2-C1-C12-C13	-1.4(6)	C1-P1-C16-C17	-92.3(4)
P1-C1-C12-C13	173.6(3)	C22-P1-C16-C17	18.6(4)
C2-C1-C12-O1	-179.5(3)	Fe1-P1-C16-C17	150.5(3)
P1-C1-C12-O1	-4.5(5)	C1-P1-C16-C21	88.6(3)
O1-C12-C13-C4	-179.2(4)	C22-P1-C16-C21	-160.5(3)
C1-C12-C13-C4	2.9(6)	Fe1-P1-C16-C21	-28.6(3)
O1-C12-C13-C9	-0.1(6)	C21-C16-C17-C18	1.0(6)
C1-C12-C13-C9	-178.1(4)	P1-C16-C17-C18	-178.1(3)
C3-C4-C13-C12	-2.2(6)	C16-C17-C18-C19	-1.9(6)
C3-C4-C13-C9	178.7(4)	C17-C18-C19-C20	1.6(6)
C10-C9-C13-C12	-104.5(4)	C18-C19-C20-C21	-0.4(6)
C11-C9-C13-C12	135.5(4)	C19-C20-C21-C16	-0.5(6)

C17-C16-C21-C20	0.2(6)	C39-C34-C35-C36	-0.9(6)
P1-C16-C21-C20	179.3(3)	P2-C34-C35-C36	174.1(3)
C1-P1-C22-C27	-164.5(3)	C34-C35-C36-C37	0.4(6)
C16-P1-C22-C27	85.9(3)	C35-C36-C37-C38	0.2(7)
Fe1-P1-C22-C27	-41.8(4)	C36-C37-C38-C39	-0.4(7)
C1-P1-C22-C23	17.8(4)	C35-C34-C39-C38	0.8(6)
C16-P1-C22-C23	-91.8(3)	P2-C34-C39-C38	-174.5(3)
Fe1-P1-C22-C23	140.5(3)	C37-C38-C39-C34	-0.1(7)
C27-C22-C23-C24	-1.4(6)	C61-P3-C40-C41	-91.9(4)
P1-C22-C23-C24	176.3(3)	C55-P3-C40-C41	16.3(4)
C22-C23-C24-C25	1.8(6)	Fe2-P3-C40-C41	136.5(3)
C23-C24-C25-C26	-1.1(6)	C61-P3-C40-C51	94.2(3)
C24-C25-C26-C27	0.1(7)	C55-P3-C40-C51	-157.5(3)
C25-C26-C27-C22	0.2(7)	Fe2-P3-C40-C51	-37.3(3)
C23-C22-C27-C26	0.4(6)	C51-C40-C41-C42	0.9(6)
P1-C22-C27-C26	-177.4(3)	P3-C40-C41-C42	-173.0(3)
C8-P2-C28-C29	-9.5(4)	C40-C41-C42-C43	2.1(6)
C34-P2-C28-C29	101.2(4)	C41-C42-C43-C52	-2.6(6)
Fe1-P2-C28-C29	-135.5(3)	C53-C44-C45-C46	-0.7(7)
C8-P2-C28-C33	174.7(3)	C44-C45-C46-C47	0.1(7)
C34-P2-C28-C33	-74.6(3)	C45-C46-C47-C54	-0.2(6)
Fe1-P2-C28-C33	48.7(4)	C45-C46-C47-P4	174.9(3)
C33-C28-C29-C30	-0.3(6)	C73-P4-C47-C46	-10.9(4)
P2-C28-C29-C30	-176.0(3)	C67-P4-C47-C46	98.6(4)
C28-C29-C30-C31	1.2(7)	Fe2-P4-C47-C46	-131.1(3)
C29-C30-C31-C32	-0.8(7)	C73-P4-C47-C54	164.2(3)
C30-C31-C32-C33	-0.5(7)	C67-P4-C47-C54	-86.3(3)
C31-C32-C33-C28	1.4(7)	Fe2-P4-C47-C54	44.0(3)
C29-C28-C33-C32	-1.0(6)	C54-O2-C51-C52	-20.7(5)
P2-C28-C33-C32	175.0(3)	C54-O2-C51-C40	159.7(3)
C28-P2-C34-C39	151.6(3)	C41-C40-C51-C52	-3.7(6)
C8-P2-C34-C39	-97.1(3)	P3-C40-C51-C52	170.5(3)
Fe1-P2-C34-C39	22.3(3)	C41-C40-C51-O2	175.9(3)
C28-P2-C34-C35	-23.4(4)	P3-C40-C51-O2	-9.9(5)
C8-P2-C34-C35	87.8(3)	O2-C51-C52-C43	-176.4(3)
Fe1-P2-C34-C35	-152.7(3)	C40-C51-C52-C43	3.2(6)

O2-C51-C52-C48	3.0(6)	C55-C56-C57-C58	0.3(6)
C40-C51-C52-C48	-177.4(4)	C56-C57-C58-C59	-0.1(7)
C42-C43-C52-C51	0.0(6)	C57-C58-C59-C60	0.3(7)
C42-C43-C52-C48	-179.3(4)	C56-C55-C60-C59	0.8(6)
C53-C48-C52-C51	13.2(5)	P3-C55-C60-C59	-179.5(3)
C49-C48-C52-C51	-106.1(4)	C58-C59-C60-C55	-0.6(6)
C50-C48-C52-C51	133.2(4)	C55-P3-C61-C62	-99.8(4)
C53-C48-C52-C43	-167.5(4)	C40-P3-C61-C62	9.8(4)
C49-C48-C52-C43	73.2(5)	Fe2-P3-C61-C62	136.4(3)
C50-C48-C52-C43	-47.5(5)	C55-P3-C61-C66	75.6(4)
C45-C44-C53-C54	1.2(6)	C40-P3-C61-C66	-174.7(3)
C45-C44-C53-C48	-178.0(4)	Fe2-P3-C61-C66	-48.2(4)
C52-C48-C53-C54	-13.3(5)	C66-C61-C62-C63	0.4(6)
C49-C48-C53-C54	106.2(4)	P3-C61-C62-C63	175.8(3)
C50-C48-C53-C54	-134.1(4)	C61-C62-C63-C64	-0.5(6)
C52-C48-C53-C44	165.9(4)	C62-C63-C64-C65	-0.1(7)
C49-C48-C53-C44	-74.7(5)	C63-C64-C65-C66	0.8(7)
C50-C48-C53-C44	45.0(5)	C64-C65-C66-C61	-0.9(7)
C44-C53-C54-O2	178.0(4)	C62-C61-C66-C65	0.3(7)
C48-C53-C54-O2	-2.8(6)	P3-C61-C66-C65	-175.3(4)
C44-C53-C54-C47	-1.3(6)	C73-P4-C67-C68	93.7(3)
C48-C53-C54-C47	177.9(4)	C47-P4-C67-C68	-15.0(4)
C51-O2-C54-C53	20.7(5)	Fe2-P4-C67-C68	-138.9(3)
C51-O2-C54-C47	-160.0(3)	C73-P4-C67-C72	-84.1(3)
C46-C47-C54-C53	0.8(6)	C47-P4-C67-C72	167.2(3)
P4-C47-C54-C53	-174.6(3)	Fe2-P4-C67-C72	43.3(3)
C46-C47-C54-O2	-178.5(3)	C72-C67-C68-C69	1.0(6)
P4-C47-C54-O2	6.0(5)	P4-C67-C68-C69	-176.7(3)
C61-P3-C55-C60	-155.6(3)	C67-C68-C69-C70	-0.1(6)
C40-P3-C55-C60	93.2(3)	C68-C69-C70-C71	-0.3(7)
Fe2-P3-C55-C60	-26.6(4)	C69-C70-C71-C72	-0.2(7)
C61-P3-C55-C56	24.0(4)	C70-C71-C72-C67	1.2(7)
C40-P3-C55-C56	-87.2(4)	C68-C67-C72-C71	-1.6(6)
Fe2-P3-C55-C56	153.0(3)	P4-C67-C72-C71	176.3(3)
C60-C55-C56-C57	-0.6(6)	C67-P4-C73-C78	158.3(3)
P3-C55-C56-C57	179.8(3)	C47-P4-C73-C78	-91.1(3)

Fe2-P4-C73-C78	26.6(4)	C73-C74-C75-C76	0.2(6)
C67-P4-C73-C74	-18.9(4)	C74-C75-C76-C77	0.1(7)
C47-P4-C73-C74	91.7(4)	C75-C76-C77-C78	-1.7(6)
Fe2-P4-C73-C74	-150.6(3)	C74-C73-C78-C77	-2.8(6)
C78-C73-C74-C75	1.1(6)	P4-C73-C78-C77	179.9(3)
P4-C73-C74-C75	178.2(3)	C76-C77-C78-C73	3.1(6)

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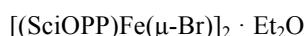
### 3.5 [FeBr(SciOPP)]<sub>2</sub>

REFERENCE NUMBER: neijk39

#### CRYSTAL STRUCTURE REPORT



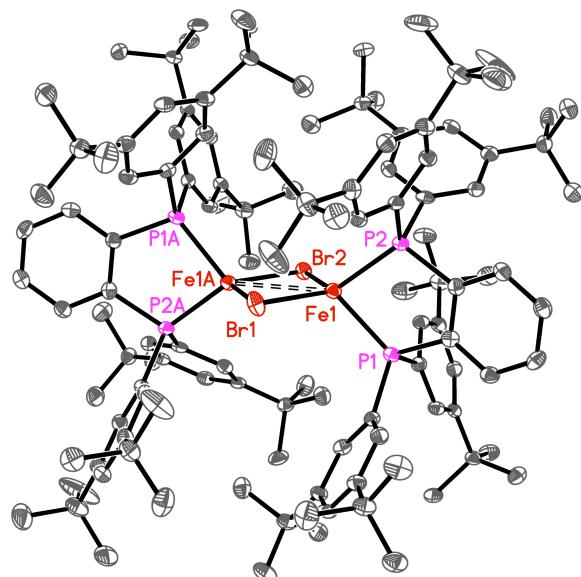
or



Report prepared for:

A. Shaps, J. Kneebone, Prof. M. Neidig

February 11, 2015



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### Data collection

A crystal ( $0.20 \times 0.18 \times 0.14 \text{ mm}^3$ ) was placed onto the tip of a thin glass optical fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at  $100.0(5) \text{ K}$ .<sup>1</sup> A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.02 cm. A randomly oriented region of reciprocal space was surveyed: five major sections of frames were collected with  $0.50^\circ$  steps in  $\omega$  at five different  $\phi$  settings and a detector position of  $-38^\circ$  in  $2\theta$ . The intensity data were corrected for absorption.<sup>2</sup> Final cell constants were calculated from the xyz centroids of 4010 strong reflections from the actual data collection after integration.<sup>3</sup> See Table 1 for additional crystal and refinement information.

### Structure solution and refinement

The structure was solved using SIR2011<sup>4</sup> and refined using SHELXL-2014/7.<sup>5</sup> The space group  $P2/n$  was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to  $R1 = 0.0527$  ( $F^2, I > 2\sigma(I)$ ) and  $wR2 = 0.1096$  ( $F^2$ , all data).

### Structure description

The structure is the one suggested. The asymmetric unit contains the metal center and one SciOPP ligand in general positions, the two bridging bromido ligands on a crystallographic two-fold axis, and one co-crystallized diethyl ether molecule on a crystallographic inversion center. One *tert*-butyl group (and its symmetry equivalent) is modeled as disordered over two positions (0.60:0.40) and the diethyl ether molecule is modeled as disordered over the crystallographic inversion center (0.50:0.50).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

<sup>1</sup> APEX3, version 2015.5-2; Bruker AXS: Madison, WI, 2015.

<sup>2</sup> Sheldrick, G. M. SADABS, version 2014/5; *J. Appl. Cryst.* **2015**, *48*, 3-10.

<sup>3</sup> SAINT, version 8.34A; Bruker AXS: Madison, WI, 2013.

<sup>4</sup> Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. SIR2011, version 1.0; *J. Appl. Cryst.* **2012**, *45*, 357-361.

<sup>5</sup> Sheldrick, G. M. SHEXL-2014/7; *Acta. Cryst.* **2015**, *C71*, 3-8.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_{\text{o}}^2 - \langle F_{\text{o}}^2 \rangle| / \Sigma |F_{\text{o}}^2|$$

$$R1 = \Sigma |F_{\text{o}}| - |F_{\text{c}}| / \Sigma |F_{\text{o}}|$$

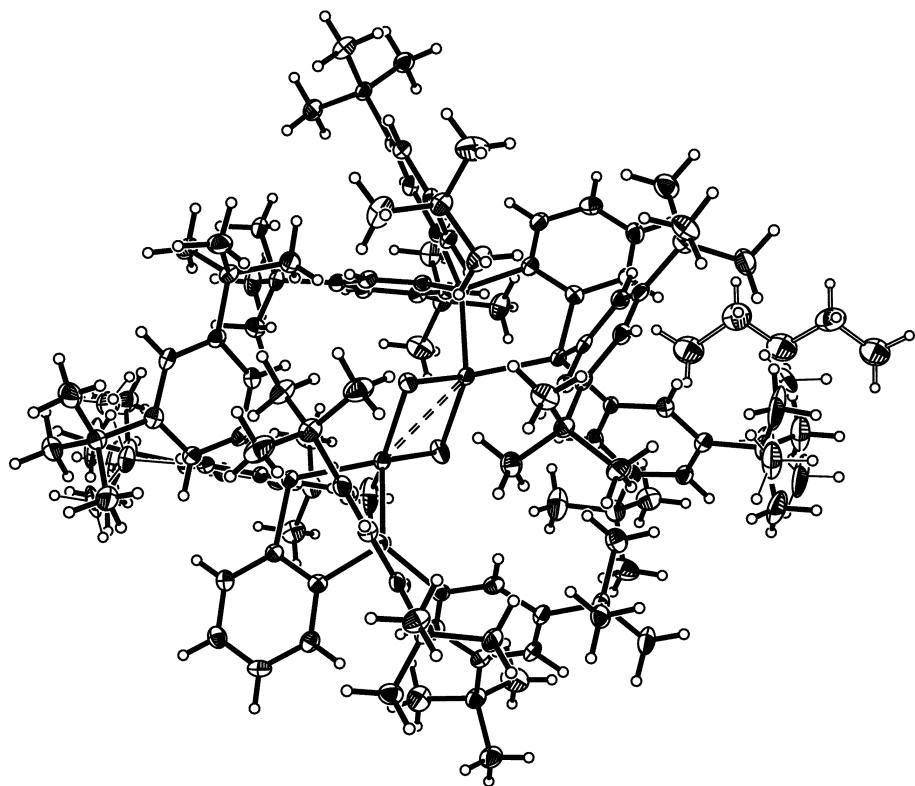
$$wR2 = [\Sigma [w(F_{\text{o}}^2 - F_{\text{c}}^2)^2] / \Sigma [w(F_{\text{o}}^2)^2]]^{1/2}$$

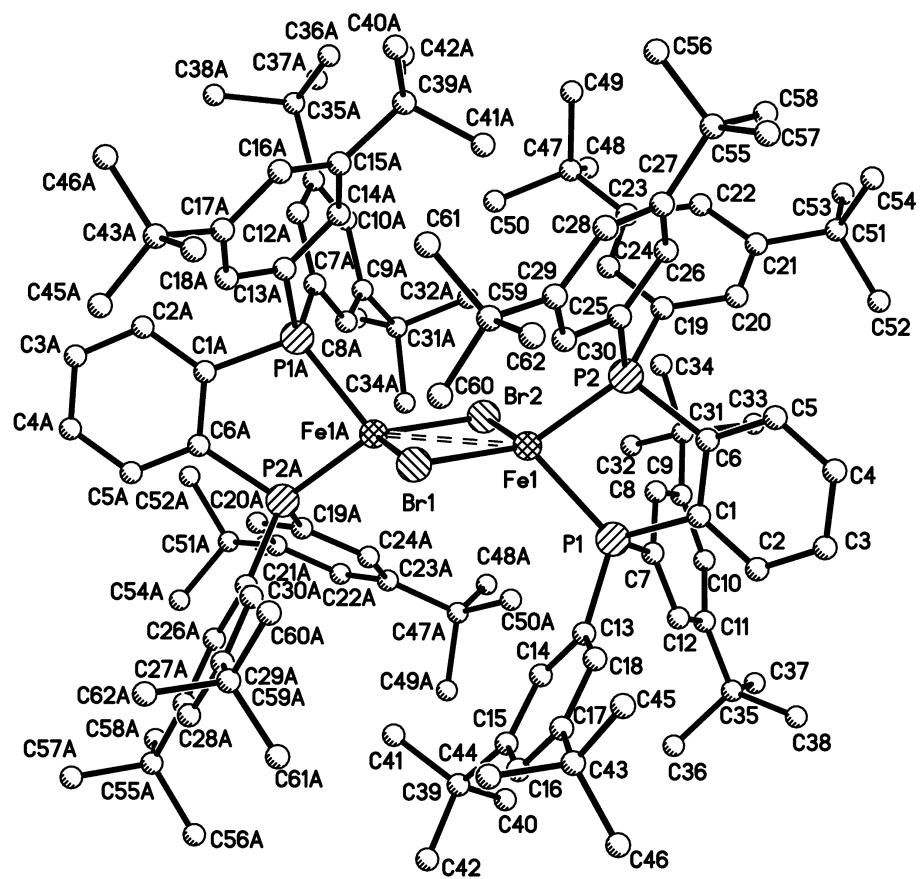
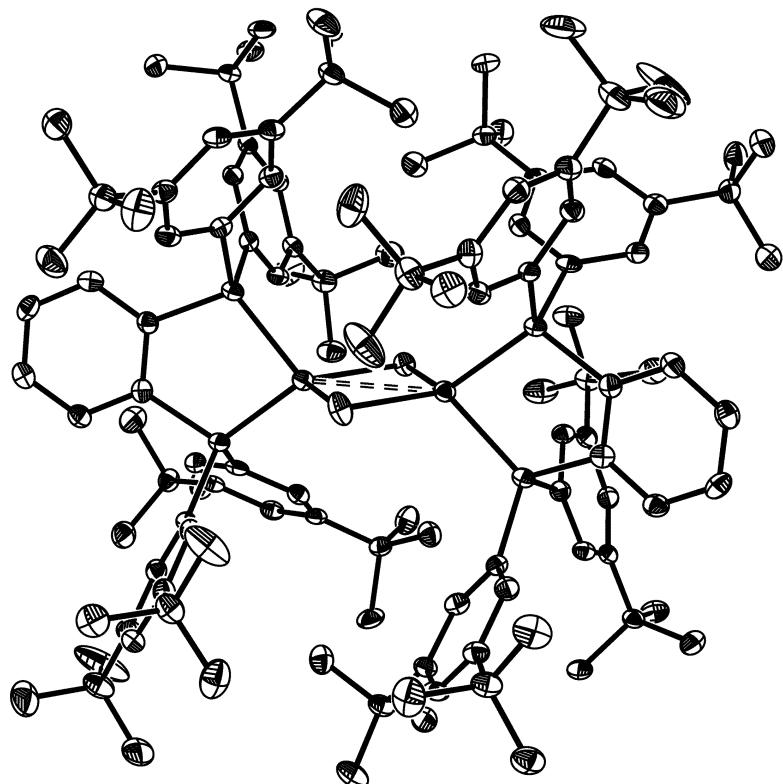
where  $w = 1 / [\sigma^2 (F_{\text{o}}^2) + (aP)^2 + bP]$  and

$$P = 1/3 \max(0, F_{\text{o}}^2) + 2/3 F_{\text{c}}^2$$

$$\text{GOF} = S = [\Sigma [w(F_{\text{o}}^2 - F_{\text{c}}^2)^2] / (m-n)]^{1/2}$$

where  $m$  = number of reflections and  $n$  = number of parameters





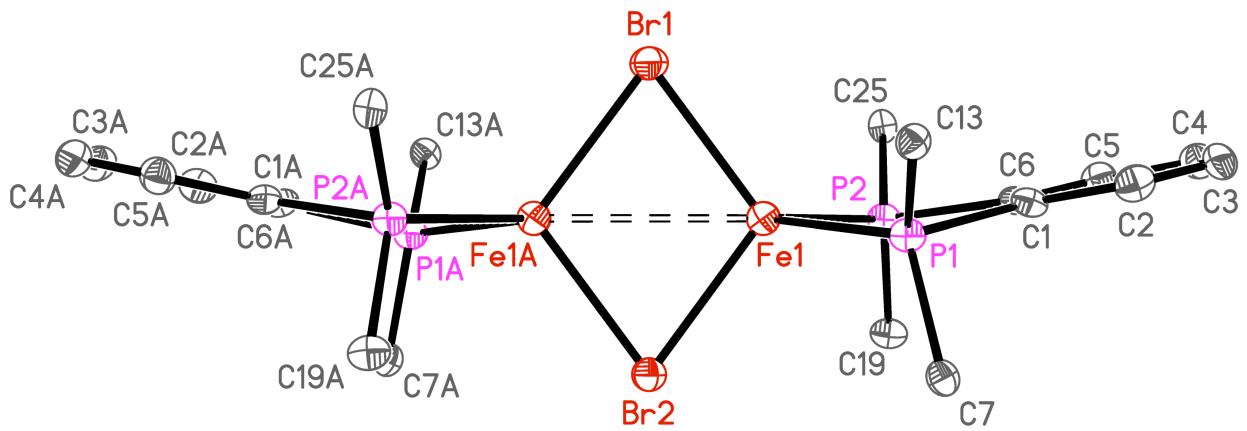
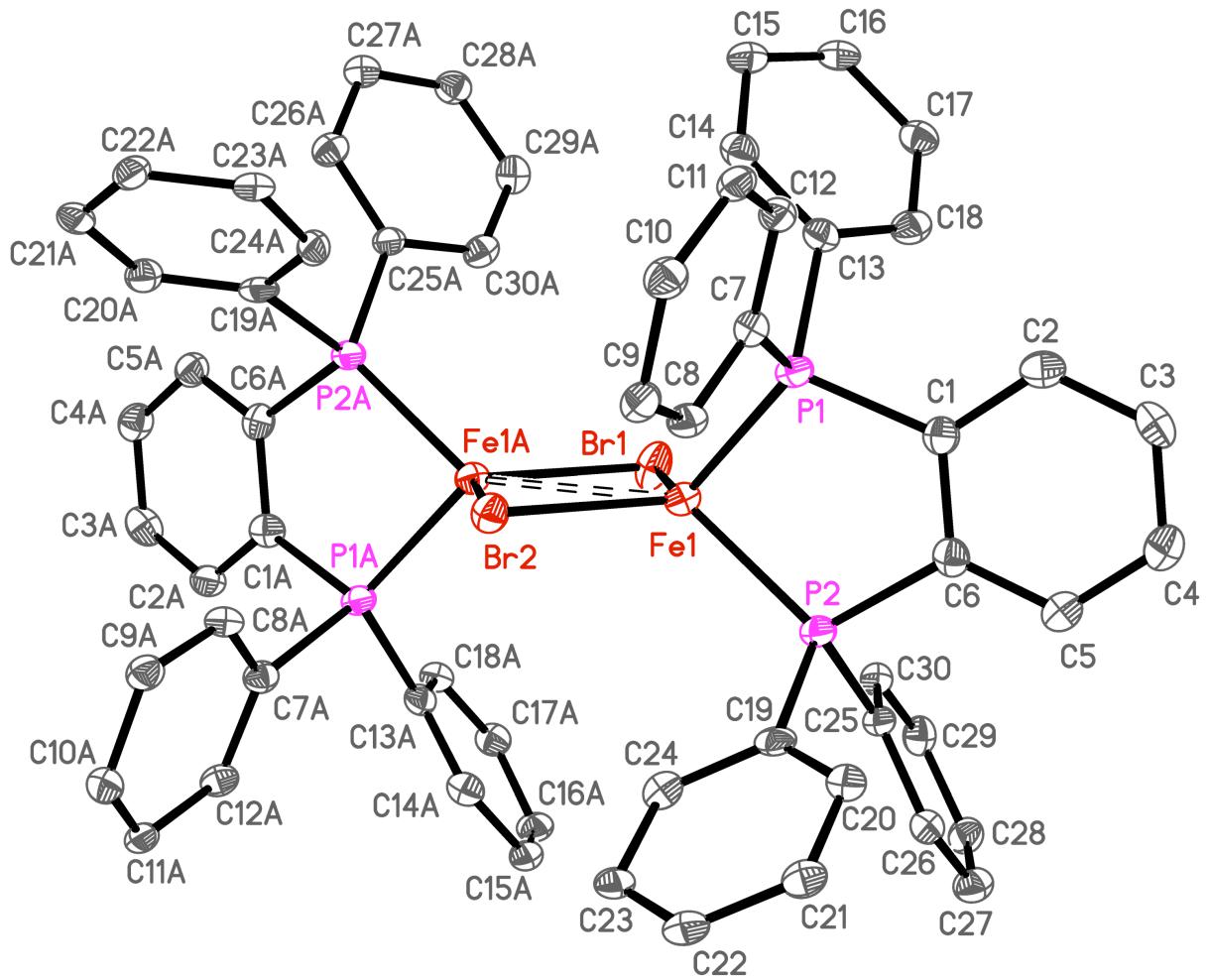


Table S25. Crystal data and structure refinement for neijk39.

Identification code	neijk39		
Empirical formula	C128 H186 Br2 Fe2 O P4		
Formula weight	2136.16		
Temperature	100.0(5) K		
Wavelength	0.71073 Å		
Crystal system	monoclinic		
Space group	<i>P2/n</i>		
Unit cell dimensions	<i>a</i> = 14.5951(11) Å	$\alpha$ = 90°	
	<i>b</i> = 14.2424(11) Å	$\beta$ = 103.2648(14)°	
	<i>c</i> = 30.373(2) Å	$\gamma$ = 90°	
Volume	6145.1(8) Å <sup>3</sup>		
<i>Z</i>	2		
Density (calculated)	1.154 Mg/m <sup>3</sup>		
Absorption coefficient	0.984 mm <sup>-1</sup>		
<i>F</i> (000)	2288		
Crystal color, morphology	dark orange, plate		
Crystal size	0.20 x 0.18 x 0.14 mm <sup>3</sup>		
Theta range for data collection	1.986 to 26.409°		
Index ranges	-18 ≤ <i>h</i> ≤ 18, -17 ≤ <i>k</i> ≤ 17, -37 ≤ <i>l</i> ≤ 37		
Reflections collected	74990		
Independent reflections	12610 [ <i>R</i> (int) = 0.1312]		
Observed reflections	7743		
Completeness to theta = 26.373°	100.0%		
Absorption correction	Multi-scan		
Max. and min. transmission	0.7454 and 0.6548		
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>		
Data / restraints / parameters	12610 / 46 / 677		
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.021		
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> 1 = 0.0527, <i>wR</i> 2 = 0.0932		
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1085, <i>wR</i> 2 = 0.1096		
Largest diff. peak and hole	0.448 and -0.421 e.Å <sup>-3</sup>		

Table S26. Atomic coordinates ( $x \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk39.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
Fe1	3248(1)	1841(1)	2254(1)	17(1)
Br1	2500	3216(1)	2500	27(1)
Br2	2500	457(1)	2500	20(1)
P1	4835(1)	1698(1)	2476(1)	17(1)
P2	3496(1)	1836(1)	1540(1)	16(1)
C1	5366(2)	1978(2)	2000(1)	18(1)
C2	6328(2)	2139(2)	2046(1)	21(1)
C3	6689(3)	2335(2)	1672(1)	24(1)
C4	6093(3)	2360(2)	1246(1)	24(1)
C5	5141(3)	2201(2)	1195(1)	21(1)
C6	4765(2)	2003(2)	1568(1)	18(1)
C7	5317(2)	511(2)	2625(1)	17(1)
C8	4766(2)	-224(2)	2401(1)	18(1)
C9	5028(2)	-1155(2)	2484(1)	19(1)
C10	5881(2)	-1327(2)	2802(1)	20(1)
C11	6459(2)	-610(2)	3022(1)	17(1)
C12	6159(2)	314(2)	2927(1)	17(1)
C13	5436(2)	2463(2)	2941(1)	17(1)
C14	5445(2)	2212(2)	3379(1)	19(1)
C15	5760(2)	2838(2)	3743(1)	19(1)
C16	6071(2)	3711(2)	3642(1)	21(1)
C17	6057(2)	4000(2)	3201(1)	20(1)
C18	5737(2)	3365(2)	2852(1)	21(1)
C19	3161(2)	742(2)	1223(1)	17(1)
C20	3697(2)	265(2)	972(1)	20(1)
C21	3367(2)	-556(2)	734(1)	19(1)
C22	2473(2)	-872(2)	755(1)	20(1)
C23	1914(2)	-423(2)	1007(1)	18(1)
C24	2281(2)	382(2)	1241(1)	18(1)
C25	2976(2)	2729(2)	1120(1)	17(1)
C26	2803(2)	2580(2)	658(1)	19(1)

C27	2440(2)	3293(3)	350(1)	22(1)
C28	2234(2)	4146(2)	525(1)	21(1)
C29	2383(2)	4323(2)	988(1)	21(1)
C30	2758(2)	3599(2)	1281(1)	19(1)
C31	4423(3)	-1974(2)	2255(1)	23(1)
C32	4046(3)	-2510(3)	2618(1)	37(1)
C33	5011(3)	-2630(3)	2035(2)	38(1)
C34	3573(3)	-1643(2)	1895(1)	29(1)
C35	7403(2)	-810(2)	3354(1)	19(1)
C36	7391(3)	-363(3)	3814(1)	29(1)
C37	7601(3)	-1861(3)	3424(1)	28(1)
C38	8200(2)	-371(3)	3172(1)	25(1)
C39	5727(3)	2536(2)	4227(1)	22(1)
C40	6305(3)	1633(2)	4345(1)	25(1)
C41	4698(3)	2341(3)	4244(1)	28(1)
C42	6124(3)	3293(3)	4577(1)	32(1)
C43	6412(3)	4983(2)	3122(1)	24(1)
C44	5835(3)	5715(3)	3315(2)	38(1)
C45	6313(3)	5182(3)	2621(1)	36(1)
C46	7460(3)	5065(3)	3365(1)	31(1)
C47	936(2)	-807(2)	1014(1)	20(1)
C48	964(3)	-1877(3)	1081(1)	30(1)
C49	268(3)	-571(3)	555(1)	29(1)
C50	548(3)	-370(3)	1396(1)	26(1)
C51	3945(3)	-1059(2)	444(1)	22(1)
C52	4987(3)	-1071(3)	680(1)	33(1)
C53	3632(3)	-2085(3)	342(1)	33(1)
C54	3807(3)	-532(3)	-9(1)	34(1)
C55	2213(5)	3140(5)	-162(2)	30(1)
C56	1158(4)	3285(6)	-365(2)	50(2)
C57	2770(6)	3854(6)	-371(2)	54(2)
C58	2466(8)	2142(5)	-277(2)	77(3)
C55'	2357(6)	3125(7)	-156(2)	30(1)
C56'	3290(6)	2796(9)	-254(3)	46(3)
C57'	1610(8)	2363(9)	-314(4)	54(2)
C58'	2040(11)	4009(8)	-439(4)	77(3)

C59	2106(3)	5276(3)	1149(1)	27(1)
C60	2326(4)	5350(3)	1667(1)	49(1)
C61	1046(3)	5434(3)	967(2)	39(1)
C62	2648(3)	6055(3)	972(1)	32(1)
C63	5014(16)	5391(10)	-731(5)	53(3)
C64	5354(7)	4663(6)	-347(3)	50(3)
O1	5040(20)	5030(30)	44(5)	53(3)
C65	5388(7)	4392(6)	430(3)	48(2)
C66	5002(16)	4844(11)	820(5)	53(3)

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Table S27. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for neijk39.

Fe(1)-P(1)	2.2681(10)	C(13)-C(14)	1.377(5)
Fe(1)-P(2)	2.2791(9)	C(13)-C(18)	1.404(5)
Fe(1)-Br(1)	2.4411(7)	C(14)-C(15)	1.412(5)
Fe(1)-Br(2)	2.4518(7)	C(14)-H(14A)	0.9500
Fe(1)-Fe(1)#1	2.9160(9)	C(15)-C(16)	1.382(5)
Br(1)-Fe(1)#1	2.4410(7)	C(15)-C(39)	1.543(5)
Br(2)-Fe(1)#1	2.4517(7)	C(16)-C(17)	1.398(5)
P(1)-C(1)	1.834(3)	C(16)-H(16A)	0.9500
P(1)-C(13)	1.839(3)	C(17)-C(18)	1.389(5)
P(1)-C(7)	1.846(3)	C(17)-C(43)	1.530(5)
P(2)-C(25)	1.836(3)	C(18)-H(18A)	0.9500
P(2)-C(19)	1.838(3)	C(19)-C(20)	1.389(5)
P(2)-C(6)	1.850(3)	C(19)-C(24)	1.396(5)
C(1)-C(2)	1.398(5)	C(20)-C(21)	1.401(5)
C(1)-C(6)	1.401(4)	C(20)-H(20A)	0.9500
C(2)-C(3)	1.388(5)	C(21)-C(22)	1.395(5)
C(2)-H(2A)	0.9500	C(21)-C(51)	1.530(5)
C(3)-C(4)	1.384(5)	C(22)-C(23)	1.397(5)
C(3)-H(3A)	0.9500	C(22)-H(22A)	0.9500
C(4)-C(5)	1.382(5)	C(23)-C(24)	1.389(5)
C(4)-H(4A)	0.9500	C(23)-C(47)	1.534(5)
C(5)-C(6)	1.394(5)	C(24)-H(24A)	0.9500
C(5)-H(5A)	0.9500	C(25)-C(26)	1.386(4)
C(7)-C(12)	1.384(4)	C(25)-C(30)	1.395(5)
C(7)-C(8)	1.399(5)	C(26)-C(27)	1.400(5)
C(8)-C(9)	1.387(5)	C(26)-H(26A)	0.9500
C(8)-H(8A)	0.9500	C(27)-C(28)	1.386(5)
C(9)-C(10)	1.410(5)	C(27)-C(55)	1.530(6)
C(9)-C(31)	1.531(5)	C(27)-C(55')	1.533(7)
C(10)-C(11)	1.394(5)	C(28)-C(29)	1.395(5)
C(10)-H(10A)	0.9500	C(28)-H(28A)	0.9500
C(11)-C(12)	1.397(5)	C(29)-C(30)	1.390(5)
C(11)-C(35)	1.536(4)	C(29)-C(59)	1.528(5)
C(12)-H(12A)	0.9500	C(30)-H(30A)	0.9500

C(31)-C(33)	1.522(5)	C(43)-C(45)	1.523(5)
C(31)-C(34)	1.528(5)	C(43)-C(44)	1.539(5)
C(31)-C(32)	1.542(5)	C(43)-C(46)	1.543(5)
C(32)-H(32A)	0.9800	C(44)-H(44A)	0.9800
C(32)-H(32B)	0.9800	C(44)-H(44B)	0.9800
C(32)-H(32C)	0.9800	C(44)-H(44C)	0.9800
C(33)-H(33A)	0.9800	C(45)-H(45A)	0.9800
C(33)-H(33B)	0.9800	C(45)-H(45B)	0.9800
C(33)-H(33C)	0.9800	C(45)-H(45C)	0.9800
C(34)-H(34A)	0.9800	C(46)-H(46A)	0.9800
C(34)-H(34B)	0.9800	C(46)-H(46B)	0.9800
C(34)-H(34C)	0.9800	C(46)-H(46C)	0.9800
C(35)-C(37)	1.529(5)	C(47)-C(50)	1.532(5)
C(35)-C(38)	1.533(5)	C(47)-C(48)	1.536(5)
C(35)-C(36)	1.538(5)	C(47)-C(49)	1.544(5)
C(36)-H(36A)	0.9800	C(48)-H(48A)	0.9800
C(36)-H(36B)	0.9800	C(48)-H(48B)	0.9800
C(36)-H(36C)	0.9800	C(48)-H(48C)	0.9800
C(37)-H(37A)	0.9800	C(49)-H(49A)	0.9800
C(37)-H(37B)	0.9800	C(49)-H(49B)	0.9800
C(37)-H(37C)	0.9800	C(49)-H(49C)	0.9800
C(38)-H(38A)	0.9800	C(50)-H(50A)	0.9800
C(38)-H(38B)	0.9800	C(50)-H(50B)	0.9800
C(38)-H(38C)	0.9800	C(50)-H(50C)	0.9800
C(39)-C(42)	1.532(5)	C(51)-C(52)	1.525(5)
C(39)-C(40)	1.535(5)	C(51)-C(54)	1.540(5)
C(39)-C(41)	1.540(5)	C(51)-C(53)	1.541(5)
C(40)-H(40A)	0.9800	C(52)-H(52A)	0.9800
C(40)-H(40B)	0.9800	C(52)-H(52B)	0.9800
C(40)-H(40C)	0.9800	C(52)-H(52C)	0.9800
C(41)-H(41A)	0.9800	C(53)-H(53A)	0.9800
C(41)-H(41B)	0.9800	C(53)-H(53B)	0.9800
C(41)-H(41C)	0.9800	C(53)-H(53C)	0.9800
C(42)-H(42A)	0.9800	C(54)-H(54A)	0.9800
C(42)-H(42B)	0.9800	C(54)-H(54B)	0.9800
C(42)-H(42C)	0.9800	C(54)-H(54C)	0.9800

C(55)-C(57)	1.529(6)	C(63)-C(64)	1.556(13)
C(55)-C(58)	1.530(6)	C(63)-H(63A)	0.9800
C(55)-C(56)	1.535(6)	C(63)-H(63B)	0.9800
C(56)-H(56A)	0.9800	C(63)-H(63C)	0.9800
C(56)-H(56B)	0.9800	C(64)-O(1)	1.46(3)
C(56)-H(56C)	0.9800	C(64)-H(64A)	0.9900
C(57)-H(57A)	0.9800	C(64)-H(64B)	0.9900
C(57)-H(57B)	0.9800	O(1)-C(65)	1.47(2)
C(57)-H(57C)	0.9800	C(65)-C(66)	1.562(13)
C(58)-H(58A)	0.9800	C(65)-H(65A)	0.9900
C(58)-H(58B)	0.9800	C(65)-H(65B)	0.9900
C(58)-H(58C)	0.9800	C(66)-H(66A)	0.9800
C(55')-C(56')	1.531(7)	C(66)-H(66B)	0.9800
C(55')-C(58')	1.534(7)	C(66)-H(66C)	0.9800
C(55')-C(57')	1.535(7)	P(1)-Fe(1)-P(2)	84.74(3)
C(56')-H(56D)	0.9800	P(1)-Fe(1)-Br(1)	118.65(3)
C(56')-H(56E)	0.9800	P(2)-Fe(1)-Br(1)	118.27(3)
C(56')-H(56F)	0.9800	P(1)-Fe(1)-Br(2)	109.45(3)
C(57')-H(57D)	0.9800	P(2)-Fe(1)-Br(2)	117.81(3)
C(57')-H(57E)	0.9800	Br(1)-Fe(1)-Br(2)	106.83(2)
C(57')-H(57F)	0.9800	P(1)-Fe(1)-Fe(1)#1	132.98(3)
C(58')-H(58D)	0.9800	P(2)-Fe(1)-Fe(1)#1	142.07(4)
C(58')-H(58E)	0.9800	Br(1)-Fe(1)-Fe(1)#1	53.323(14)
C(58')-H(58F)	0.9800	Br(2)-Fe(1)-Fe(1)#1	53.510(14)
C(59)-C(62)	1.528(5)	Fe(1)#1-Br(1)-Fe(1)	73.35(3)
C(59)-C(60)	1.535(5)	Fe(1)#1-Br(2)-Fe(1)	72.98(3)
C(59)-C(61)	1.535(5)	C(1)-P(1)-C(13)	105.24(15)
C(60)-H(60A)	0.9800	C(1)-P(1)-C(7)	100.81(15)
C(60)-H(60B)	0.9800	C(13)-P(1)-C(7)	105.44(15)
C(60)-H(60C)	0.9800	C(1)-P(1)-Fe(1)	109.46(11)
C(61)-H(61A)	0.9800	C(13)-P(1)-Fe(1)	116.70(11)
C(61)-H(61B)	0.9800	C(7)-P(1)-Fe(1)	117.43(11)
C(61)-H(61C)	0.9800	C(25)-P(2)-C(19)	101.86(15)
C(62)-H(62A)	0.9800	C(25)-P(2)-C(6)	101.13(15)
C(62)-H(62B)	0.9800	C(19)-P(2)-C(6)	106.00(15)
C(62)-H(62C)	0.9800	C(25)-P(2)-Fe(1)	121.84(11)

C(19)-P(2)-Fe(1)	114.85(11)	C(7)-C(12)-H(12A)	119.4
C(6)-P(2)-Fe(1)	109.38(11)	C(11)-C(12)-H(12A)	119.4
C(2)-C(1)-C(6)	119.3(3)	C(14)-C(13)-C(18)	119.3(3)
C(2)-C(1)-P(1)	123.5(3)	C(14)-C(13)-P(1)	119.1(3)
C(6)-C(1)-P(1)	117.2(2)	C(18)-C(13)-P(1)	120.7(3)
C(3)-C(2)-C(1)	120.7(3)	C(13)-C(14)-C(15)	121.4(3)
C(3)-C(2)-H(2A)	119.6	C(13)-C(14)-H(14A)	119.3
C(1)-C(2)-H(2A)	119.6	C(15)-C(14)-H(14A)	119.3
C(4)-C(3)-C(2)	119.8(3)	C(16)-C(15)-C(14)	117.4(3)
C(4)-C(3)-H(3A)	120.1	C(16)-C(15)-C(39)	123.1(3)
C(2)-C(3)-H(3A)	120.1	C(14)-C(15)-C(39)	119.5(3)
C(5)-C(4)-C(3)	120.0(3)	C(15)-C(16)-C(17)	123.0(3)
C(5)-C(4)-H(4A)	120.0	C(15)-C(16)-H(16A)	118.5
C(3)-C(4)-H(4A)	120.0	C(17)-C(16)-H(16A)	118.5
C(4)-C(5)-C(6)	121.1(3)	C(18)-C(17)-C(16)	117.8(3)
C(4)-C(5)-H(5A)	119.5	C(18)-C(17)-C(43)	122.9(3)
C(6)-C(5)-H(5A)	119.5	C(16)-C(17)-C(43)	119.3(3)
C(5)-C(6)-C(1)	119.1(3)	C(17)-C(18)-C(13)	121.0(3)
C(5)-C(6)-P(2)	124.4(3)	C(17)-C(18)-H(18A)	119.5
C(1)-C(6)-P(2)	116.4(2)	C(13)-C(18)-H(18A)	119.5
C(12)-C(7)-C(8)	119.7(3)	C(20)-C(19)-C(24)	118.8(3)
C(12)-C(7)-P(1)	125.4(3)	C(20)-C(19)-P(2)	125.9(3)
C(8)-C(7)-P(1)	115.0(2)	C(24)-C(19)-P(2)	115.3(3)
C(9)-C(8)-C(7)	121.5(3)	C(19)-C(20)-C(21)	121.4(3)
C(9)-C(8)-H(8A)	119.2	C(19)-C(20)-H(20A)	119.3
C(7)-C(8)-H(8A)	119.2	C(21)-C(20)-H(20A)	119.3
C(8)-C(9)-C(10)	117.1(3)	C(22)-C(21)-C(20)	117.4(3)
C(8)-C(9)-C(31)	122.6(3)	C(22)-C(21)-C(51)	121.3(3)
C(10)-C(9)-C(31)	120.3(3)	C(20)-C(21)-C(51)	121.2(3)
C(11)-C(10)-C(9)	122.9(3)	C(21)-C(22)-C(23)	123.2(3)
C(11)-C(10)-H(10A)	118.6	C(21)-C(22)-H(22A)	118.4
C(9)-C(10)-H(10A)	118.6	C(23)-C(22)-H(22A)	118.4
C(10)-C(11)-C(12)	117.7(3)	C(24)-C(23)-C(22)	116.9(3)
C(10)-C(11)-C(35)	122.2(3)	C(24)-C(23)-C(47)	122.6(3)
C(12)-C(11)-C(35)	120.1(3)	C(22)-C(23)-C(47)	120.5(3)
C(7)-C(12)-C(11)	121.1(3)	C(23)-C(24)-C(19)	122.3(3)

C(23)-C(24)-H(24A)	118.9	H(33A)-C(33)-H(33B)	109.5
C(19)-C(24)-H(24A)	118.9	C(31)-C(33)-H(33C)	109.5
C(26)-C(25)-C(30)	119.2(3)	H(33A)-C(33)-H(33C)	109.5
C(26)-C(25)-P(2)	123.2(3)	H(33B)-C(33)-H(33C)	109.5
C(30)-C(25)-P(2)	117.6(2)	C(31)-C(34)-H(34A)	109.5
C(25)-C(26)-C(27)	121.2(3)	C(31)-C(34)-H(34B)	109.5
C(25)-C(26)-H(26A)	119.4	H(34A)-C(34)-H(34B)	109.5
C(27)-C(26)-H(26A)	119.4	C(31)-C(34)-H(34C)	109.5
C(28)-C(27)-C(26)	117.5(3)	H(34A)-C(34)-H(34C)	109.5
C(28)-C(27)-C(55)	120.0(4)	H(34B)-C(34)-H(34C)	109.5
C(26)-C(27)-C(55)	122.4(4)	C(37)-C(35)-C(38)	108.3(3)
C(28)-C(27)-C(55')	123.2(5)	C(37)-C(35)-C(11)	112.6(3)
C(26)-C(27)-C(55')	119.1(5)	C(38)-C(35)-C(11)	109.1(3)
C(27)-C(28)-C(29)	123.2(3)	C(37)-C(35)-C(36)	108.7(3)
C(27)-C(28)-H(28A)	118.4	C(38)-C(35)-C(36)	109.1(3)
C(29)-C(28)-H(28A)	118.4	C(11)-C(35)-C(36)	109.0(3)
C(30)-C(29)-C(28)	117.3(3)	C(35)-C(36)-H(36A)	109.5
C(30)-C(29)-C(59)	123.3(3)	C(35)-C(36)-H(36B)	109.5
C(28)-C(29)-C(59)	119.4(3)	H(36A)-C(36)-H(36B)	109.5
C(29)-C(30)-C(25)	121.5(3)	C(35)-C(36)-H(36C)	109.5
C(29)-C(30)-H(30A)	119.2	H(36A)-C(36)-H(36C)	109.5
C(25)-C(30)-H(30A)	119.2	H(36B)-C(36)-H(36C)	109.5
C(33)-C(31)-C(34)	108.8(3)	C(35)-C(37)-H(37A)	109.5
C(33)-C(31)-C(9)	110.0(3)	C(35)-C(37)-H(37B)	109.5
C(34)-C(31)-C(9)	112.3(3)	H(37A)-C(37)-H(37B)	109.5
C(33)-C(31)-C(32)	109.9(3)	C(35)-C(37)-H(37C)	109.5
C(34)-C(31)-C(32)	107.5(3)	H(37A)-C(37)-H(37C)	109.5
C(9)-C(31)-C(32)	108.5(3)	H(37B)-C(37)-H(37C)	109.5
C(31)-C(32)-H(32A)	109.5	C(35)-C(38)-H(38A)	109.5
C(31)-C(32)-H(32B)	109.5	C(35)-C(38)-H(38B)	109.5
H(32A)-C(32)-H(32B)	109.5	H(38A)-C(38)-H(38B)	109.5
C(31)-C(32)-H(32C)	109.5	C(35)-C(38)-H(38C)	109.5
H(32A)-C(32)-H(32C)	109.5	H(38A)-C(38)-H(38C)	109.5
H(32B)-C(32)-H(32C)	109.5	H(38B)-C(38)-H(38C)	109.5
C(31)-C(33)-H(33A)	109.5	C(42)-C(39)-C(40)	109.1(3)
C(31)-C(33)-H(33B)	109.5	C(42)-C(39)-C(41)	108.6(3)

C(40)-C(39)-C(41)	109.2(3)	H(45A)-C(45)-H(45B)	109.5
C(42)-C(39)-C(15)	112.1(3)	C(43)-C(45)-H(45C)	109.5
C(40)-C(39)-C(15)	108.8(3)	H(45A)-C(45)-H(45C)	109.5
C(41)-C(39)-C(15)	109.0(3)	H(45B)-C(45)-H(45C)	109.5
C(39)-C(40)-H(40A)	109.5	C(43)-C(46)-H(46A)	109.5
C(39)-C(40)-H(40B)	109.5	C(43)-C(46)-H(46B)	109.5
H(40A)-C(40)-H(40B)	109.5	H(46A)-C(46)-H(46B)	109.5
C(39)-C(40)-H(40C)	109.5	C(43)-C(46)-H(46C)	109.5
H(40A)-C(40)-H(40C)	109.5	H(46A)-C(46)-H(46C)	109.5
H(40B)-C(40)-H(40C)	109.5	H(46B)-C(46)-H(46C)	109.5
C(39)-C(41)-H(41A)	109.5	C(50)-C(47)-C(23)	111.8(3)
C(39)-C(41)-H(41B)	109.5	C(50)-C(47)-C(48)	107.9(3)
H(41A)-C(41)-H(41B)	109.5	C(23)-C(47)-C(48)	111.0(3)
C(39)-C(41)-H(41C)	109.5	C(50)-C(47)-C(49)	109.2(3)
H(41A)-C(41)-H(41C)	109.5	C(23)-C(47)-C(49)	107.8(3)
H(41B)-C(41)-H(41C)	109.5	C(48)-C(47)-C(49)	109.1(3)
C(39)-C(42)-H(42A)	109.5	C(47)-C(48)-H(48A)	109.5
C(39)-C(42)-H(42B)	109.5	C(47)-C(48)-H(48B)	109.5
H(42A)-C(42)-H(42B)	109.5	H(48A)-C(48)-H(48B)	109.5
C(39)-C(42)-H(42C)	109.5	C(47)-C(48)-H(48C)	109.5
H(42A)-C(42)-H(42C)	109.5	H(48A)-C(48)-H(48C)	109.5
H(42B)-C(42)-H(42C)	109.5	H(48B)-C(48)-H(48C)	109.5
C(45)-C(43)-C(17)	111.6(3)	C(47)-C(49)-H(49A)	109.5
C(45)-C(43)-C(44)	108.7(3)	C(47)-C(49)-H(49B)	109.5
C(17)-C(43)-C(44)	109.0(3)	H(49A)-C(49)-H(49B)	109.5
C(45)-C(43)-C(46)	108.8(3)	C(47)-C(49)-H(49C)	109.5
C(17)-C(43)-C(46)	109.1(3)	H(49A)-C(49)-H(49C)	109.5
C(44)-C(43)-C(46)	109.6(3)	H(49B)-C(49)-H(49C)	109.5
C(43)-C(44)-H(44A)	109.5	C(47)-C(50)-H(50A)	109.5
C(43)-C(44)-H(44B)	109.5	C(47)-C(50)-H(50B)	109.5
H(44A)-C(44)-H(44B)	109.5	H(50A)-C(50)-H(50B)	109.5
C(43)-C(44)-H(44C)	109.5	C(47)-C(50)-H(50C)	109.5
H(44A)-C(44)-H(44C)	109.5	H(50A)-C(50)-H(50C)	109.5
H(44B)-C(44)-H(44C)	109.5	H(50B)-C(50)-H(50C)	109.5
C(43)-C(45)-H(45A)	109.5	C(52)-C(51)-C(21)	111.0(3)
C(43)-C(45)-H(45B)	109.5	C(52)-C(51)-C(54)	109.6(3)

C(21)-C(51)-C(54)	108.0(3)	H(57A)-C(57)-H(57B)	109.5
C(52)-C(51)-C(53)	107.5(3)	C(55)-C(57)-H(57C)	109.5
C(21)-C(51)-C(53)	112.6(3)	H(57A)-C(57)-H(57C)	109.5
C(54)-C(51)-C(53)	108.1(3)	H(57B)-C(57)-H(57C)	109.5
C(51)-C(52)-H(52A)	109.5	C(55)-C(58)-H(58A)	109.5
C(51)-C(52)-H(52B)	109.5	C(55)-C(58)-H(58B)	109.5
H(52A)-C(52)-H(52B)	109.5	H(58A)-C(58)-H(58B)	109.5
C(51)-C(52)-H(52C)	109.5	C(55)-C(58)-H(58C)	109.5
H(52A)-C(52)-H(52C)	109.5	H(58A)-C(58)-H(58C)	109.5
H(52B)-C(52)-H(52C)	109.5	H(58B)-C(58)-H(58C)	109.5
C(51)-C(53)-H(53A)	109.5	C(56')-C(55')-C(27)	111.9(6)
C(51)-C(53)-H(53B)	109.5	C(56')-C(55')-C(58')	108.0(7)
H(53A)-C(53)-H(53B)	109.5	C(27)-C(55')-C(58')	112.1(7)
C(51)-C(53)-H(53C)	109.5	C(56')-C(55')-C(57')	108.8(7)
H(53A)-C(53)-H(53C)	109.5	C(27)-C(55')-C(57')	108.1(7)
H(53B)-C(53)-H(53C)	109.5	C(58')-C(55')-C(57')	107.7(7)
C(51)-C(54)-H(54A)	109.5	C(55')-C(56')-H(56D)	109.5
C(51)-C(54)-H(54B)	109.5	C(55')-C(56')-H(56E)	109.5
H(54A)-C(54)-H(54B)	109.5	H(56D)-C(56')-H(56E)	109.5
C(51)-C(54)-H(54C)	109.5	C(55')-C(56')-H(56F)	109.5
H(54A)-C(54)-H(54C)	109.5	H(56D)-C(56')-H(56F)	109.5
H(54B)-C(54)-H(54C)	109.5	H(56E)-C(56')-H(56F)	109.5
C(57)-C(55)-C(58)	110.1(6)	C(55')-C(57')-H(57D)	109.5
C(57)-C(55)-C(27)	108.4(5)	C(55')-C(57')-H(57E)	109.5
C(58)-C(55)-C(27)	110.9(5)	H(57D)-C(57')-H(57E)	109.5
C(57)-C(55)-C(56)	108.9(5)	C(55')-C(57')-H(57F)	109.5
C(58)-C(55)-C(56)	107.9(6)	H(57D)-C(57')-H(57F)	109.5
C(27)-C(55)-C(56)	110.6(5)	H(57E)-C(57')-H(57F)	109.5
C(55)-C(56)-H(56A)	109.5	C(55')-C(58')-H(58D)	109.5
C(55)-C(56)-H(56B)	109.5	C(55')-C(58')-H(58E)	109.5
H(56A)-C(56)-H(56B)	109.5	H(58D)-C(58')-H(58E)	109.5
C(55)-C(56)-H(56C)	109.5	C(55')-C(58')-H(58F)	109.5
H(56A)-C(56)-H(56C)	109.5	H(58D)-C(58')-H(58F)	109.5
H(56B)-C(56)-H(56C)	109.5	H(58E)-C(58')-H(58F)	109.5
C(55)-C(57)-H(57A)	109.5	C(29)-C(59)-C(62)	109.7(3)
C(55)-C(57)-H(57B)	109.5	C(29)-C(59)-C(60)	112.3(3)

C(62)-C(59)-C(60)	107.9(3)	H(63A)-C(63)-H(63B)	109.5
C(29)-C(59)-C(61)	109.5(3)	C(64)-C(63)-H(63C)	109.5
C(62)-C(59)-C(61)	109.1(3)	H(63A)-C(63)-H(63C)	109.5
C(60)-C(59)-C(61)	108.3(3)	H(63B)-C(63)-H(63C)	109.5
C(59)-C(60)-H(60A)	109.5	O(1)-C(64)-C(63)	105.6(16)
C(59)-C(60)-H(60B)	109.5	O(1)-C(64)-H(64A)	110.6
H(60A)-C(60)-H(60B)	109.5	C(63)-C(64)-H(64A)	110.6
C(59)-C(60)-H(60C)	109.5	O(1)-C(64)-H(64B)	110.6
H(60A)-C(60)-H(60C)	109.5	C(63)-C(64)-H(64B)	110.6
H(60B)-C(60)-H(60C)	109.5	H(64A)-C(64)-H(64B)	108.8
C(59)-C(61)-H(61A)	109.5	C(64)-O(1)-C(65)	108(2)
C(59)-C(61)-H(61B)	109.5	O(1)-C(65)-C(66)	103.5(14)
H(61A)-C(61)-H(61B)	109.5	O(1)-C(65)-H(65A)	111.1
C(59)-C(61)-H(61C)	109.5	C(66)-C(65)-H(65A)	111.1
H(61A)-C(61)-H(61C)	109.5	O(1)-C(65)-H(65B)	111.1
H(61B)-C(61)-H(61C)	109.5	C(66)-C(65)-H(65B)	111.1
C(59)-C(62)-H(62A)	109.5	H(65A)-C(65)-H(65B)	109.0
C(59)-C(62)-H(62B)	109.5	C(65)-C(66)-H(66A)	109.5
H(62A)-C(62)-H(62B)	109.5	C(65)-C(66)-H(66B)	109.5
C(59)-C(62)-H(62C)	109.5	H(66A)-C(66)-H(66B)	109.5
H(62A)-C(62)-H(62C)	109.5	C(65)-C(66)-H(66C)	109.5
H(62B)-C(62)-H(62C)	109.5	H(66A)-C(66)-H(66C)	109.5
C(64)-C(63)-H(63A)	109.5	H(66B)-C(66)-H(66C)	109.5
C(64)-C(63)-H(63B)	109.5		

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y,-z+1/2

Table S28. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk39. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^{*} b^{*} U_{12} ]$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Fe1	18(1)	18(1)	15(1)	1(1)	3(1)	1(1)
Br1	40(1)	18(1)	28(1)	0	18(1)	0
Br2	22(1)	18(1)	20(1)	0	7(1)	0
P1	19(1)	17(1)	14(1)	0(1)	2(1)	0(1)
P2	17(1)	17(1)	14(1)	0(1)	1(1)	0(1)
C1	21(2)	12(2)	19(2)	2(1)	4(2)	-2(2)
C2	22(2)	20(2)	19(2)	1(1)	1(2)	2(2)
C3	17(2)	20(2)	32(2)	1(2)	4(2)	-2(2)
C4	28(2)	21(2)	23(2)	1(2)	9(2)	-1(2)
C5	24(2)	21(2)	18(2)	1(1)	6(2)	2(2)
C6	21(2)	13(2)	21(2)	-2(1)	6(2)	-2(1)
C7	17(2)	20(2)	15(2)	1(1)	4(2)	-1(2)
C8	18(2)	21(2)	14(2)	2(1)	0(2)	0(2)
C9	22(2)	19(2)	16(2)	2(1)	5(2)	0(2)
C10	21(2)	19(2)	19(2)	2(1)	5(2)	2(2)
C11	18(2)	22(2)	12(2)	1(1)	3(1)	1(2)
C12	19(2)	17(2)	14(2)	-1(1)	2(2)	-5(2)
C13	15(2)	18(2)	18(2)	-1(1)	1(2)	1(2)
C14	19(2)	16(2)	21(2)	1(1)	1(2)	-1(2)
C15	20(2)	21(2)	16(2)	-3(1)	1(2)	2(2)
C16	21(2)	23(2)	16(2)	-4(1)	-1(2)	-1(2)
C17	19(2)	18(2)	21(2)	-2(1)	1(2)	-2(2)
C18	21(2)	23(2)	17(2)	3(1)	2(2)	5(2)
C19	21(2)	17(2)	11(2)	3(1)	-2(2)	1(2)
C20	19(2)	23(2)	16(2)	0(1)	2(2)	-1(2)
C21	21(2)	18(2)	16(2)	4(1)	0(2)	5(2)
C22	24(2)	18(2)	14(2)	-2(1)	1(2)	1(2)
C23	18(2)	22(2)	13(2)	2(1)	-2(1)	0(2)
C24	22(2)	16(2)	16(2)	1(1)	4(2)	5(2)
C25	15(2)	22(2)	12(2)	0(1)	2(1)	-1(2)
C26	19(2)	20(2)	19(2)	-1(1)	4(2)	-4(2)

C27	23(2)	25(2)	18(2)	1(2)	3(2)	1(2)
C28	23(2)	23(2)	19(2)	4(2)	4(2)	1(2)
C29	22(2)	19(2)	24(2)	2(2)	8(2)	-1(2)
C30	20(2)	22(2)	16(2)	-1(1)	5(2)	-4(2)
C31	28(2)	16(2)	24(2)	0(2)	2(2)	-1(2)
C32	38(2)	31(2)	36(2)	6(2)	-2(2)	-13(2)
C33	33(2)	27(2)	50(3)	-17(2)	-1(2)	3(2)
C34	33(2)	22(2)	26(2)	-2(2)	-3(2)	-3(2)
C35	20(2)	21(2)	13(2)	2(1)	0(2)	1(2)
C36	21(2)	44(3)	17(2)	-1(2)	-3(2)	3(2)
C37	26(2)	24(2)	28(2)	6(2)	-3(2)	1(2)
C38	20(2)	29(2)	26(2)	5(2)	2(2)	-1(2)
C39	27(2)	24(2)	14(2)	1(1)	2(2)	-1(2)
C40	27(2)	31(2)	18(2)	5(2)	4(2)	2(2)
C41	30(2)	27(2)	28(2)	2(2)	10(2)	6(2)
C42	45(3)	35(2)	16(2)	-2(2)	4(2)	-3(2)
C43	30(2)	19(2)	23(2)	0(2)	3(2)	-5(2)
C44	44(3)	16(2)	58(3)	-4(2)	20(2)	-2(2)
C45	48(3)	27(2)	31(2)	8(2)	6(2)	-8(2)
C46	36(2)	28(2)	29(2)	-3(2)	6(2)	-11(2)
C47	18(2)	19(2)	19(2)	-2(1)	1(2)	-1(2)
C48	27(2)	25(2)	38(2)	-5(2)	9(2)	-7(2)
C49	19(2)	40(3)	24(2)	-4(2)	-4(2)	-1(2)
C50	28(2)	26(2)	24(2)	-1(2)	7(2)	-4(2)
C51	21(2)	23(2)	23(2)	-4(2)	7(2)	-2(2)
C52	29(2)	41(3)	30(2)	-9(2)	7(2)	1(2)
C53	33(2)	31(2)	40(2)	-9(2)	17(2)	0(2)
C54	32(2)	48(3)	26(2)	-4(2)	11(2)	-2(2)
C55	42(3)	28(2)	18(2)	-2(2)	4(2)	4(2)
C56	43(5)	78(7)	20(4)	8(4)	-8(3)	-21(5)
C57	51(5)	89(6)	23(4)	-2(4)	9(3)	-26(4)
C58	149(9)	65(5)	11(3)	-2(3)	6(5)	32(6)
C55'	42(3)	28(2)	18(2)	-2(2)	4(2)	4(2)
C56'	42(7)	80(9)	21(6)	-7(5)	19(5)	17(6)
C57'	51(5)	89(6)	23(4)	-2(4)	9(3)	-26(4)
C58'	149(9)	65(5)	11(3)	-2(3)	6(5)	32(6)

C59	34(2)	21(2)	26(2)	1(2)	9(2)	3(2)
C60	94(4)	26(2)	29(2)	1(2)	20(3)	16(2)
C61	34(2)	27(2)	61(3)	0(2)	21(2)	1(2)
C62	37(2)	18(2)	40(2)	-2(2)	7(2)	1(2)
C63	57(4)	41(5)	61(5)	-4(6)	17(4)	4(4)
C64	43(6)	43(6)	65(7)	15(5)	11(5)	8(5)
O1	57(4)	41(5)	61(5)	-4(6)	17(4)	4(4)
C65	45(6)	42(6)	60(6)	16(5)	18(5)	-3(5)
C66	57(4)	41(5)	61(5)	-4(6)	17(4)	4(4)

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Table S29. Hydrogen coordinates ( $x \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for neijk39.

	x	y	z	U(eq)
H2A	6740	2114	2338	25
H3A	7343	2451	1707	28
H4A	6339	2487	988	28
H5A	4735	2227	902	25
H8A	4199	-83	2186	22
H10A	6070	-1960	2868	23
H12A	6540	816	3072	20
H14A	5234	1604	3439	23
H16A	6306	4134	3883	25
H18A	5722	3544	2549	25
H20A	4301	501	961	23
H22A	2233	-1419	589	23
H24A	1920	699	1418	22
H26A	2934	1982	547	23
H28A	1979	4633	320	26
H30A	2869	3699	1598	23
H32A	4575	-2721	2858	55
H32B	3681	-3056	2480	55
H32C	3641	-2094	2747	55
H33A	5263	-2281	1811	58
H33B	4615	-3146	1885	58
H33C	5532	-2884	2267	58
H34A	3790	-1289	1661	43
H34B	3177	-1238	2035	43
H34C	3208	-2188	1757	43
H36A	6861	-617	3925	43
H36B	7321	319	3779	43
H36C	7982	-507	4031	43
H37A	7639	-2149	3136	41
H37B	7091	-2156	3536	41

H37C	8198	-1951	3646	41
H38A	8231	-675	2886	38
H38B	8800	-460	3392	38
H38C	8080	301	3121	38
H40A	6963	1756	4338	38
H40B	6050	1143	4124	38
H40C	6273	1423	4648	38
H41A	4675	2112	4545	41
H41B	4431	1866	4017	41
H41C	4331	2922	4180	41
H42A	6775	3434	4565	48
H42B	6109	3066	4880	48
H42C	5742	3863	4511	48
H44A	5168	5656	3163	57
H44B	6057	6347	3265	57
H44C	5911	5608	3640	57
H45A	5645	5194	2467	54
H45B	6632	4688	2488	54
H45C	6599	5791	2584	54
H46A	7530	4950	3690	47
H46B	7688	5697	3320	47
H46C	7827	4600	3241	47
H48A	1445	-2036	1352	45
H48B	1115	-2180	817	45
H48C	348	-2096	1116	45
H49A	279	107	502	44
H49B	-373	-767	559	44
H49C	477	-903	313	44
H50A	986	-490	1687	38
H50B	-65	-650	1397	38
H50C	475	308	1347	38
H52A	5218	-425	729	50
H52B	5341	-1403	490	50
H52C	5071	-1393	972	50
H53A	2986	-2097	158	50
H53B	3660	-2420	627	50

H53C	4052	-2391	176	50
H54A	4017	119	48	52
H54B	3140	-542	-164	52
H54C	4178	-839	-199	52
H56A	1022	3162	-691	74
H56B	985	3934	-312	74
H56C	794	2853	-221	74
H57A	2638	3760	-700	81
H57B	3444	3768	-243	81
H57C	2584	4491	-306	81
H58A	2180	1690	-105	115
H58B	3152	2066	-198	115
H58C	2230	2029	-601	115
H56D	3760	3295	-173	69
H56E	3196	2649	-576	69
H56F	3509	2234	-75	69
H57D	1535	2255	-639	81
H57E	1009	2568	-254	81
H57F	1810	1779	-149	81
H58D	2532	4489	-364	115
H58E	1458	4248	-371	115
H58F	1929	3853	-761	115
H60A	3005	5281	1788	73
H60B	1992	4852	1789	73
H60C	2120	5963	1754	73
H61A	695	4930	1075	59
H61B	899	5433	636	59
H61C	867	6040	1075	59
H62A	3325	5963	1091	48
H62B	2461	6666	1072	48
H62C	2504	6036	641	48
H63A	5206	5185	-1005	79
H63B	5297	6004	-637	79
H63C	4327	5442	-795	79
H64A	5073	4039	-436	61
H64B	6048	4604	-276	61

H65A	6084	4369	508	58
H65B	5139	3748	363	58
H66A	5262	4511	1103	79
H66B	4314	4798	748	79
H66C	5189	5506	853	79

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Table S30. Torsion angles [°] for neijk39.

C13-P1-C1-C2	40.6(3)	C31-C9-C10-C11	-179.7(3)
C7-P1-C1-C2	-68.9(3)	C9-C10-C11-C12	1.5(5)
Fe1-P1-C1-C2	166.7(3)	C9-C10-C11-C35	-177.8(3)
C13-P1-C1-C6	-141.3(3)	C8-C7-C12-C11	-1.8(5)
C7-P1-C1-C6	109.2(3)	P1-C7-C12-C11	179.3(3)
Fe1-P1-C1-C6	-15.1(3)	C10-C11-C12-C7	0.1(5)
C6-C1-C2-C3	0.9(5)	C35-C11-C12-C7	179.3(3)
P1-C1-C2-C3	179.0(3)	C1-P1-C13-C14	-157.7(3)
C1-C2-C3-C4	-0.8(5)	C7-P1-C13-C14	-51.6(3)
C2-C3-C4-C5	0.7(5)	Fe1-P1-C13-C14	80.7(3)
C3-C4-C5-C6	-0.8(5)	C1-P1-C13-C18	33.5(3)
C4-C5-C6-C1	0.9(5)	C7-P1-C13-C18	139.6(3)
C4-C5-C6-P2	176.9(3)	Fe1-P1-C13-C18	-88.1(3)
C2-C1-C6-C5	-0.9(5)	C18-C13-C14-C15	-0.8(5)
P1-C1-C6-C5	-179.2(2)	P1-C13-C14-C15	-169.7(3)
C2-C1-C6-P2	-177.3(2)	C13-C14-C15-C16	-0.8(5)
P1-C1-C6-P2	4.5(3)	C13-C14-C15-C39	178.1(3)
C25-P2-C6-C5	-38.3(3)	C14-C15-C16-C17	2.1(5)
C19-P2-C6-C5	67.6(3)	C39-C15-C16-C17	-176.8(3)
Fe1-P2-C6-C5	-168.1(3)	C15-C16-C17-C18	-1.7(5)
C25-P2-C6-C1	137.8(3)	C15-C16-C17-C43	179.7(3)
C19-P2-C6-C1	-116.3(3)	C16-C17-C18-C13	0.1(5)
Fe1-P2-C6-C1	8.1(3)	C43-C17-C18-C13	178.6(3)
C1-P1-C7-C12	89.0(3)	C14-C13-C18-C17	1.1(5)
C13-P1-C7-C12	-20.3(3)	P1-C13-C18-C17	169.9(3)
Fe1-P1-C7-C12	-152.2(3)	C25-P2-C19-C20	92.3(3)
C1-P1-C7-C8	-89.9(3)	C6-P2-C19-C20	-13.1(3)
C13-P1-C7-C8	160.8(3)	Fe1-P2-C19-C20	-133.9(3)
Fe1-P1-C7-C8	28.9(3)	C25-P2-C19-C24	-87.1(3)
C12-C7-C8-C9	2.2(5)	C6-P2-C19-C24	167.5(2)
P1-C7-C8-C9	-178.8(3)	Fe1-P2-C19-C24	46.6(3)
C7-C8-C9-C10	-0.7(5)	C24-C19-C20-C21	0.8(5)
C7-C8-C9-C31	177.8(3)	P2-C19-C20-C21	-178.6(2)
C8-C9-C10-C11	-1.1(5)	C19-C20-C21-C22	0.6(5)

C19-C20-C21-C51	177.9(3)	C12-C11-C35-C37	178.6(3)
C20-C21-C22-C23	-1.5(5)	C10-C11-C35-C38	118.1(3)
C51-C21-C22-C23	-178.8(3)	C12-C11-C35-C38	-61.1(4)
C21-C22-C23-C24	0.9(5)	C10-C11-C35-C36	-122.8(3)
C21-C22-C23-C47	179.8(3)	C12-C11-C35-C36	57.9(4)
C22-C23-C24-C19	0.7(5)	C16-C15-C39-C42	-2.9(5)
C47-C23-C24-C19	-178.2(3)	C14-C15-C39-C42	178.2(3)
C20-C19-C24-C23	-1.5(5)	C16-C15-C39-C40	-123.6(4)
P2-C19-C24-C23	178.0(3)	C14-C15-C39-C40	57.6(4)
C19-P2-C25-C26	-25.6(3)	C16-C15-C39-C41	117.4(4)
C6-P2-C25-C26	83.5(3)	C14-C15-C39-C41	-61.5(4)
Fe1-P2-C25-C26	-155.1(2)	C18-C17-C43-C45	3.3(5)
C19-P2-C25-C30	155.1(3)	C16-C17-C43-C45	-178.2(3)
C6-P2-C25-C30	-95.7(3)	C18-C17-C43-C44	123.4(4)
Fe1-P2-C25-C30	25.6(3)	C16-C17-C43-C44	-58.1(4)
C30-C25-C26-C27	1.8(5)	C18-C17-C43-C46	-117.0(4)
P2-C25-C26-C27	-177.5(3)	C16-C17-C43-C46	61.6(4)
C25-C26-C27-C28	-1.8(5)	C24-C23-C47-C50	-15.2(4)
C25-C26-C27-C55	-178.0(4)	C22-C23-C47-C50	165.9(3)
C25-C26-C27-C55'	173.7(5)	C24-C23-C47-C48	-135.7(3)
C26-C27-C28-C29	0.9(5)	C22-C23-C47-C48	45.4(4)
C55-C27-C28-C29	177.2(4)	C24-C23-C47-C49	104.8(4)
C55'-C27-C28-C29	-174.5(5)	C22-C23-C47-C49	-74.0(4)
C27-C28-C29-C30	0.1(5)	C22-C21-C51-C52	-142.3(3)
C27-C28-C29-C59	-178.1(3)	C20-C21-C51-C52	40.6(4)
C28-C29-C30-C25	-0.1(5)	C22-C21-C51-C54	97.5(4)
C59-C29-C30-C25	178.0(3)	C20-C21-C51-C54	-79.6(4)
C26-C25-C30-C29	-0.8(5)	C22-C21-C51-C53	-21.7(5)
P2-C25-C30-C29	178.5(3)	C20-C21-C51-C53	161.2(3)
C8-C9-C31-C33	127.5(4)	C28-C27-C55-C57	61.0(7)
C10-C9-C31-C33	-54.0(4)	C26-C27-C55-C57	-122.9(5)
C8-C9-C31-C34	6.2(5)	C28-C27-C55-C58	-178.0(6)
C10-C9-C31-C34	-175.2(3)	C26-C27-C55-C58	-1.9(8)
C8-C9-C31-C32	-112.4(4)	C28-C27-C55-C56	-58.3(7)
C10-C9-C31-C32	66.2(4)	C26-C27-C55-C56	117.8(5)
C10-C11-C35-C37	-2.2(5)	C28-C27-C55'-C56'	122.6(7)

C26-C27-C55'-C56'	-52.7(9)	C30-C29-C59-C60	2.3(5)
C28-C27-C55'-C58'	1.0(9)	C28-C29-C59-C60	-179.7(4)
C26-C27-C55'-C58'	-174.3(7)	C30-C29-C59-C61	-118.1(4)
C28-C27-C55'-C57'	-117.6(7)	C28-C29-C59-C61	60.0(4)
C26-C27-C55'-C57'	67.2(8)	C63-C64-O1-C65	-176.8(14)
C30-C29-C59-C62	122.1(4)	C64-O1-C65-C66	-179.5(13)
C28-C29-C59-C62	-59.8(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y,-z+1/2